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(54) Title: SYNERGISTIC COMBINATION OF SILK PROTEINS

(54) Bezeichnung: SYNERGISTISCHE KOMBINATION VON SEIDENPROTEINEN

(57) Abstract: Disclosed are cosmetic preparations containing a synergistically effective active substance complex made of sericine and fibroin and/or the derivatives thereof for the treatment of skin and hair.

(57) Zusammenfassung: Es werden kosmetische Zubereitungen enthaltend einen synergistisch wirkenden Wirkstoffkomplex aus Sericin und Fibroin und/oder deren Derivaten zur Behandlung von Haut und Haaren beschrieben.

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SYNERGISTIC COMBINATION OF SILK PROTEINS

The invention relates to cosmetic compositions comprising a synergistic active combination of silk proteins as well as the use of these compositions to clean and/or care for skin and hair. Furthermore, the use of this inventive combination of silk proteins in hair colorants is described.

Cosmetic treatment of skin and hair is an important part of human body care. Nowadays, human hair is treated in many different ways with hair-care preparations. Such treatments include, for instance, the cleaning of hair with shampoos, the care and regeneration with rinses and treatments as well as bleaching, coloring and setting of hair with colorants, tints, waving formulations and styling preparations. Among these, formulations for modifying or shading the color of the hair play a prominent role. Disregarding bleaching agents, which produce an oxidative lightening of the hair by degradation of the natural hair dyes, the three most important types of hair colorants in the field of hair coloration are:

So-called oxidation colorants are used for permanent, intensive colorations with corresponding fastness properties. Such oxidation colorants normally contain oxidation dye precursors, so-called developer components and coupler components. Under the influence of oxidizing agents or atmospheric oxygen, or by coupling with one or more coupler components, the developer components

form the actual dyestuffs with one another. Oxidation colorants are distinguished by excellent long-lasting coloring results. However, natural-looking colorations normally require a mixture of a relatively large number of oxidation dye precursors; in many cases, additional substantive dyes are used for shading. If the dyes formed during the coloration process or those used directly have markedly different fastness properties (e.g. UV stability, perspiration fastness, wash fastness etc.), then over time a noticeable and thus undesirable color change may result. This phenomenon arises to a greater extent if the hairstyle has hair or regions of hair with varying degrees of damage. An example of this is with long hair, where the ends have been subjected to all possible environmental influences over a long period of time and are generally markedly more damaged than the regions of relatively freshly grown hair.

For temporary colorations, colorants or tints containing substantive dyes as their coloring component are normally used. Substantive dyes are based on dye molecules which are directly absorbed onto the hair and do not require an oxidative process for developing the color. Dyes such as these include, for example, henna which has been used since ancient times for coloring the body and hair. These colorations are generally much more sensitive to shampooing than are oxidative colorations, so that an often-unwanted change of shade or even a visible "discoloration" can occur much more quickly. A further disadvantage of such temporary colorations is due to the fact that they are incremental to the natural hair tones and thus only permit shades that are darker than the starting tones. Consequently, colorants based on substantive dyestuffs are also usually used in combination with preparations of oxidizing agents so that the starting shade of the fibers is lightened as well as actually colored.

Consequently, both processes require the addition of strong oxidizing agents such as hydrogen peroxide solutions, which in certain cases can damage the hair being dyed. Suitable hair care products must then be used to counteract this damage.

Finally, a new type of dyeing process has recently attracted great interest. In this process, precursors of the natural hair dye melanin are applied on the hair and then, as a result of the oxidation process, form dyes that are analogous to natural dyes. Such a process, using 5,6-dihydroxy indoline as the dye precursor, has been described in EP-B1-530 229. In the case of particularly repeated use of compositions containing 5,6-dihydroxy indoline, people with gray hair can regain their natural hair color. The coloration can occur with oxygen in the air as the sole oxidizing agent and thus no further oxidizing agents are needed. For people whose natural hair is medium blond to brown, indoline can be used as the sole dye precursor. For natural red heads and particularly those people with darker to black hair however, satisfactory results can often be obtained only with the use of additional dye components, especially specific precursors of oxidation dyes.

Last but not least, the heavy demands made on hair from dyeing or permanent waving for example, and also from shampooing and environmental pollution, mean that care products with the longest possible prolonged action are becoming increasingly important. Care products of this type influence the natural structure and the properties of hair. Such treatments can subsequently optimize the wet- and dry combing properties of hair, for example, the behavior and fullness of the hair, or protect hair from increased splitting.

Accordingly, it has become customary to subject hair to a special after-care treatment. Thus, hair is treated with special active substances, for example quaternary ammonium salts or special polymers, usually in the form of a rinse. According to the formulation, such treatment can improve the combing properties, the behavior and the fullness of the hair and reduce the number of split ends.

Further, so-called combination preparations have recently been developed with the aim of reducing the cost of typical multi-step processes, especially those for direct usage by the consumer.

These preparations comprise, besides the usual components e.g. for cleaning or dyeing hair, additional active substances that were previously restricted to hair after-care products. Consequently the consumer economizes an application step and simultaneously the packaging expenses are reduced because one less product is used.

In general, the available active substances for both after-care compositions and also for combination preparations act preferably at the hair surface. Thus, active substances are known that lend the hair gloss, behavior, fullness, better wet- and dry combing properties or prevent splitting. However, as equally as important as the outer appearance of the hair is the inner structural cohesion of the hair fibers, which can be strongly influenced - especially by oxidative and reductive processes like dyeing and permanent waving.

However, the known active substances cannot satisfactorily cover all requirements. There still remains a need for active substances or combinations of active substances for cosmetics with good care properties and good biodegradation properties. Particularly with dyestuff formulations and/or formulations containing electrolytes, there remains a need for additional active substances for care-products which can be added to known formulations without any problem.

Active care products are sought, particularly protein hydrolyzates, which can significantly improve the internal structure of fibers, particularly keratinous fibers. Structure strengthening, that is restructuring in the sense of the invention, is understood to mean a reduction in the damage to keratinous fibers resulting from all the various causes. Here, for example, the reconstitution of the natural strength plays an important part. Restructured fibers are characterized,

for example, by an improved gloss or by an improved feel or by easier combing. In addition, they exhibit an optimized strength and elasticity. A successful restructuring can be physically observed as an increased melting point compared with that of damaged fibers. The higher the melting point of the hair, the stronger is the fiber structure. An exact description of the method to determine the melting region of hair can be found in DE 196 173 95 A1.

Protein hydrolyzates and their use in cosmetics are well known and often used in cosmetic compositions. Reference may be made to the pertinent technical literature, for example A. Domsch, "Die kosmetischen Präparate" Volume II, pages 205 *et seq.*, Verlag für die chemische Industrie, H. Ziolkowsky. However, no indication is to be found of restructuring, which is characterized by an improved strength and elasticity.

It has been known for a long time to add proteins or modified proteins to cosmetic preparations to produce care effects. Either water-soluble proteins or proteins modified by chemical and/or enzymatic reactions and thus rendered water-soluble have been used for this purpose. Precisely with those reactions to achieve adequate water solubility, such an extensive degradation of fiber proteins is required that the cosmetic activity is often no longer satisfactory.

Silk is a very interesting fiber protein for cosmetics. Silk is understood to mean the fibers of the cocoon of the silk moth (*Bombyx mori L.*). The raw silk fiber consists of a double stranded fibroin. Sericin acts as a gum to hold the double strands together. Silk consists of 70-80 wt.% fibroin, 19-28 wt.% sericin, 0.5-1 wt.% fat and 0.5-1 wt.% colorants and mineral constituents.

The important constituents of sericin are hydroxyamino acids with ca. 46 wt.%. Sericin consists of a group of 5 to 6 proteins. The important amino acids of sericin are serine (Ser, 37 wt.%), aspartic acid (Asp, 26 wt.%), glycine (Gly, 17 wt.%), alanine (Ala), leucine (Leu) and tyrosine (Tyr).

The water-insoluble fibroin is counted as part of the scleroproteins with long chain molecular structure. The major constituents of fibroin are glycine (44 wt.%), alanine (26 wt.%) and tyrosine (13 wt.%). A further important structural characteristic of fibroin is the hexapeptide sequence Ser-Gly-Ala-Gly-Ala-Gly.

Technically, it is possible to easily separate both the silk proteins from each other. It is not surprising that both sericin and fibroin are each known as distinct raw materials for use in cosmetic products. Moreover, protein hydrolyzates and derivatives of each individual silk protein are known raw materials for cosmetic compositions. Thus, sericin for example, is marketed as such by Pentapharm Ltd. as the commercial product sericin code 303-02. Fibroin is far more frequently offered in the market as protein hydrolyzate with different molecular weights. These hydrolyzates are marketed particularly as "silk hydrolyzates". For example, hydrolyzed fibroin with an average molecular weight between 350 and 1000 is marketed under the commercial name Promois® Silk. Colloidal fibroin solutions are also described in DE 31 39 438 A1 as additives in cosmetic compositions.

The positive properties of the silk protein derivatives from sericin and fibroin are each known from the literature. The sales brochure of Pentapharm describes the cosmetic effect of sericin on the skin as relieving, moisturizing and film forming. The properties of a shampoo comprising sericin as a care component are reported in "Aertzlichen Kosmetologie 17, 91-110 (1987)" by W.Engel et al. The effect of a fibroin derivative is, for example described in DE 31 39 438 A1 as caring and vivifying for hair. However in none of the cited journals can be found even the slightest indication of a synergistic increase in the positive effects of the silk proteins and their derivatives by the simultaneous use of sericin and fibroin or of their derivatives and/or hydrolyzates.

Surprisingly, it has now been found that by the use of sericin and fibroin and/or their derivatives, the properties of skin and hair can be significantly increased

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when treated with preparations comprising such a combination of active substances.

According to a first aspect, the invention provides cosmetic preparations comprising an active ingredient complex (A) consisting of:

(a) an active ingredient (A1) which is chosen from sericin and/or derivatives thereof and/or mixtures thereof, and

(b) an active ingredient (A2) which is chosen from fibroin and/or derivatives thereof and/or mixtures thereof.

According to a second aspect, the invention provides an agent for dyeing keratin fibres comprising, in a cosmetically acceptable carrier, an active ingredient complex (A) according to the first aspect, and

(a) at least one dye precursor (DP) and

(b) an amphoteric polymer (AP).

According to a third aspect, the invention provides a two-component agent for dyeing keratin fibres consisting of a first component (C1) comprising at least one dye precursor (DP), and a second component (C2) comprising at least one active ingredient complex (A) according to the first aspect, wherein at least one of the two components comprises at least one amphoteric polymer (AP).

According to a fourth aspect, the invention provides a three-component agent for dyeing keratin fibres consisting of a first component (C1) comprising at least one dye precursor (DP), a second component (C2) comprising at least one active ingredient complex (A) according to the first aspect and a third component (C3) comprising at least one oxidizing agent, wherein at least one of the two components (C1) or (C2) comprises at least one amphoteric polymer (AP).

According to a fifth aspect, the invention provides a method of dyeing keratin fibres wherein one of the agents according to the second, third or fourth aspects is applied to the fibres, left there for a contact time and then rinsed off.

According to a sixth aspect, the invention provides use of a cosmetic preparation according to the first aspect for the cleaning and/or care of skin and hair.

According to a seventh aspect, the invention provides use of a cosmetic preparation according to the first aspect for the restructuring of keratin fibres, in particular human hair.

According to an eighth aspect, the invention provides a method of treating skin or hair in which a preparation according to the first aspect is applied to said skin or hair, the preparation being rinsed out again after a contact time of from 1 to 45 minutes.

According to a ninth aspect, the invention provides dyed keratin fibres produced in accordance with the method of the fifth aspect.

Accordingly, cosmetic preparations comprising an active substance complex (A) consisting of the active substance (A1) selected from sericin, sericin hydrolyzates and/or their derivatives, as well as mixtures thereof, and an active substance (A2) selected from fibroin and/or fibroin hydrolyzates and/or their derivatives and/or mixtures thereof are disclosed herein.

The inventive active substance complex (A) significantly improves in a synergistic manner the previously described, important, internal and external structural characteristics and the strength and elasticity of human hair.

According to the invention, the active substances (A1) used in the active substance complex (A) are:

- natural sericin,
- hydrolyzed and/or further derivatized sericin, for example, commercial products with the INCI designations sericin, hydrolysed sericin, or hydrolyzed silk,
- a mixture of the amino acids serine, aspartic acid and glycine and/or their methyl-, propyl-, iso-propyl-, butyl-, iso-butyl esters, their salts such as, for example, hydrochlorides, sulfates, acetates, citrates, tartrates, wherein this mixture comprises serine and/or its derivatives in 20 to 60 wt.%, aspartic acid and/or its derivatives in 10 to 40 wt.% and glycine and/or its derivatives in 5 to 30 wt.%, with the proviso that the quantities of these amino acids and/or their derivatives preferably make up 100 wt.%,
- as well as their mixtures.

According to the invention, the active substances (A2) used in the active substance complex (A) are:

- natural fibroin converted into a soluble form,

- hydrolyzed and/or further derivatized fibroin, particularly partially hydrolyzed fibroin comprising as the major constituent the amino acid sequence Ser-Gly-Ala-Gly-Ala-Gly,
- the amino acid sequence Ser-Gly-Ala-Gly-Ala-Gly,
- a mixture of amino acids glycine, alanine and tyrosine and/or their methyl-, propyl-, iso-propyl-, butyl-, iso-butyl esters, their salts, such as for example hydrochlorides, sulfates, acetates, citrates, tartrates, wherein this mixture comprises glycine and/or its derivatives in 20 to 60 wt.%, alanine and/or its derivatives in 10 to 40 wt.% and tyrosine and/or its derivatives in 0 to 25 wt.%, with the proviso that the quantities of these amino acids and/or their derivatives preferably make up 100 wt.%,
- as well as their mixtures.

According to the invention, it can be preferred that one of the two active substance components of the active substance complex (A) is used in the natural or at best solublized form. According to the invention it is also possible to use a mixture of a plurality of active substances (A1) and/or (A2).

According to the invention it can be preferable that both the active substances (A1) and (A2) are used in the inventive preparations in the proportion from 10:90 to 70:30, particularly 15:85 to 50:50 and most preferably 20:80 to 40:60, based on each of their contents of active substances.

The derivatives of the hydrolyzates of sericin and fibroin include both anionic as well as cationic protein hydrolyzates. The inventive protein hydrolyzates of sericin and fibroin together with the derivatives prepared from them can be obtained from the corresponding proteins by a chemical, particularly alkaline or acidic, hydrolysis, by an enzymatic hydrolysis and/or by a combination of both types of hydrolysis. The hydrolysis of proteins generally affords a protein hydrolyzate with a molecular weight distribution of about 100 Daltons, up to several thousand Daltons. Preferred are such protein hydrolyzates from sericin and fibroin and/or their derivatives that are based on a protein content with a

molecular weight of 100 to 25000 Daltons, preferably 250 to 10000 Daltons. Further, cationic protein hydrolyzates of sericin and fibroin are also understood to mean quaternized amino acids and their mixtures. Quaternization of the protein hydrolyzates or the amino acids is often carried out with quaternary ammonium salts such as for example N,N-dimethyl-N-(n-alkyl)-N-(2-hydroxy-3-chloro-n-propyl)-ammonium halides. Moreover, the cationic protein hydrolyzates can be still further derivatized. Typical examples of the inventive cationic protein hydrolyzates and their derivatives would be those named in the INCI designations in the "International Cosmetic Ingredient Dictionary and Handbook", (seventh edition 1997, The Cosmetic, Toiletry and Fragrance Association 1101 17th Street, N.W., Suite 300, Washington DC 20036-4702) and the commercially available products: cocodimonium hydroxypropyl hydrolyzed silk, cocodimonium hydroxypropyl silk amino acids, hydroxypropyltrimonium hydrolyzed silk, lauryldimonium hydroxypropyl hydrolyzed silk, steardimonium hydroxypropyl hydrolyzed silk, quaternium-79 hydrolyzed silk. Typical examples of the inventive anionic protein hydrolyzates and their derivatives would be those named in the INCI designations in the "International Cosmetic Ingredient Dictionary and Handbook", (seventh edition 1997, The Cosmetic, Toiletry and Fragrance Association 1101 17th Street, N.W., Suite 300, Washington DC 20036-4702) and the commercially available products: potassium cocoyl hydrolyzed silk, sodium lauroyl hydrolyzed silk or sodium stearoyl hydrolyzed silk. Lastly, typical examples of the inventive useable derivatives of sericin and fibroin would be those commercially available products named under the INCI designations: ethyl ester of hydrolyzed silk and hydrolyzed silk PG-propyl methylsilanediol. Further inventive useable, if not necessarily preferred, commercially available products are with the INCI designations: palmitoyl oligopeptide, palmitoyl pentapeptide-3, palmitoyl pentapeptide-2, acetyl hexapeptide-1, acetyl hexapeptide-3, copper tripeptide-1, hexapeptide-1, hexapeptide-2, MEA-hydrolyzed silk.

The inventive active substances comprise the active substance complex (A) in quantities from 0.001 – 10 wt.% based on the total composition. Quantities from 0.005 to 5, particularly 0.01 to 3 wt.% are quite particularly preferred.

In a preferred embodiment of the invention, the effect of the inventive active substance complex (A) can be further increased by fats (D). By fats are meant fatty acids, fatty alcohols, natural and synthetic waxes, which can be present in both solid form as well as liquids in aqueous dispersion, and natural and synthetic cosmetic oil components.

The fatty acids (D1) that can be used are straight chained and/or branched, saturated or unsaturated fatty acids with 6 - 30 carbon atoms. Fatty acids with 10 - 22 carbon atoms are preferred. Hereunder, could be cited the isostearic acids, such as the commercial products Emersol® 871 and Emersol® 875, and isopalmitic acids, such as the commercial product Edenor® IP 95, as well as other commercial fatty acids marketed by Cognis under the trade name Edenor®. Further typical examples of such fatty acids are caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid, and technical-grade mixtures thereof which are produced, for example, during the pressurized cleavage of natural fats and oils, the oxidation of aldehydes from the Roelen Oxo Synthesis or the dimerization of unsaturated fatty acids. Normally, fatty acid fractions obtained from cocoa oil or palm oil are particularly preferred; generally, the use of stearic acid is especially preferred.

The amount added is 0.1 – 15 wt.%, based on the total composition. Amounts of 0.5 – 10 wt.% are preferred, and amounts of 1 – 5 wt.% can be quite particularly advantageous.

The added fatty alcohols (D2) can be saturated, mono or polyunsaturated, branched or linear fatty alcohols with $C_6 - C_{30}$, preferably $C_{10} - C_{22}$ and quite particularly preferably $C_{12} - C_{22}$ carbon atoms. In terms of the invention, there can be used for example, decanol, octanol, octenol, dodecanol, decenol, octadienol, dodecadienol, decadienol, oleyl alcohol, erucyl alcohol, ricinyl alcohol, stearyl alcohol, isostearyl alcohol, cetyl alcohol, lauryl alcohol, myristyl alcohol, arachyl alcohol, caprylic alcohol, caproic alcohol, capric alcohol, linolyl alcohol, linolenyl alcohol and behenyl alcohol, as well as their Guerbet alcohols, this list being exemplary and non-limiting. However, the fatty alcohols are preferably derived from naturally occurring fatty acids, and are normally obtained by reduction of the esters of fatty acids. According to the invention, such fatty alcohol fractions can be used that are obtained from the reduction of naturally occurring triglycerides like beef tallow, palm oil, peanut oil, colza oil, cotton seed oil, soy oil, sunflower oil, and linseed oil, or from fatty acid esters resulting from their products of transesterification with suitable alcohols, and thus a mixture of different fatty alcohols. Such products that can be purchased are, for example, Stenol®, eg Stenol® 1618 or Lanette®, eg Lanette® O or Lorol®, eg Lorol® C8, Lorol® C14, Lorol® C18, Lorol® C8-18, HD-Ocenol®, Crodacol®, eg Crodacol® CS, Novol®, Eutanol® G, Guerbitol® 16, Guerbitol® 18, Guerbitol® 20, Isofol®12, Isofol® 16, Isofol® 24, Isofol® 36, Isocarb® 12, Isocarb® 16 or Isocarb® 24. Of course, according to the invention, wool wax alcohols can also be used, such as, for example those purchased under the designations Corona®, White Swan®, Coronet® or Fluilan®. The fatty alcohols are added in quantities of 0.1 – 30 wt.% based on the total composition, preferably in quantities of 0.1 – 20 wt.%.

The natural or synthetic waxes (D3) that can be used according to the invention are solid paraffins or isoparaffins, carnuba waxes, beeswaxes, candelilla waxes, ozokerite, ceresine, spermaceti, sunflower wax, fruit waxes such as for example apple wax or citrus wax, microwaxes from PE or PP. Such waxes can be obtained from Kahl & Co., Trittau, for example.

The addition quantities are 0.1 – 50 wt.% based on the total composition, preferably 0.1 – 20 wt.% and particularly preferably 0.1 – 15 wt.%, based on the total composition.

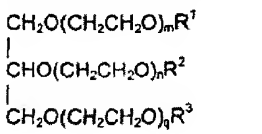
The natural and synthetic cosmetic oils (D4) that can increase the effect of the inventive active substance complex (A) include, for example:

- vegetal oils. Examples of such oils are sunflower oil, olive oil, soybean oil, rapeseed oil, almond oil, jojoba oil, orange oil, wheat germ oil, peach kernel oil and the liquid fractions of coconut oil. Also suitable, however, are other triglyceride oils, such as the liquid fractions of beef tallow and synthetic triglyceride oils.
- liquid paraffin oils and synthetic hydrocarbons as well as di-n-alkyl ethers with a total of between 12 and 36 carbon atoms, in particular 12 and 24 carbon atoms, such as, for example, di-n-octyl ether, di-n-decyl ether, di-n-nonyl ether, di-n-undecyl ether, di-n-dodecyl ether, n-hexyl n-octyl ether, n-octyl n-decyl ether, n-decyl n-undecyl ether, n-undecyl n-dodecyl ether and n-hexyl n-undecyl ether and di-tert-butyl ether, diisopentyl ether, di-3-ethyldecyl ether, tert-butyl n-octyl ether, isopentyl n-octyl ether and 2-methylpentyl n-octyl ether. The compounds 1,3-di(2-ethylhexyl)cyclohexane (Cetiol® S) and di-n-octyl ether (Cetiol® OE), which are available as commercial products, may be preferred.
- ester oils. By ester oils are meant esters of C_6-C_{30} fatty acids with C_2-C_{30} fatty alcohols. Preference is given to the monoesters of fatty acids with alcohols having 2 to 24 carbon atoms. Examples of the fatty acid part used in the esters are caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid, and technical-grade mixtures thereof which are produced, for example, during the pressurized cleavage of natural fats and oils, the oxidation of aldehydes from the Roelen Oxo synthesis or the dimerization of unsaturated fatty acids, with alcohols. Examples of the fatty

alcohol part in the ester oils are isopropyl alcohol, caproic alcohol, caprylic alcohol, 2-ethylhexyl alcohol, capric alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linolyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol, and technical-grade mixtures thereof which are produced, for example, during the high-pressure hydrogenation of technical-grade methyl esters based on fats and oils or aldehydes from the Roelen Oxo synthesis, and as the monomer fraction during the dimerization of unsaturated fatty alcohols. Particularly preferred according to the invention are isopropyl myristate (Rilanit® IPM), C16-C18 alkyl ester of isononanoic acid (Cetiol® SN), 2-ethylhexyl palmitate (Cegesoft® 24), 2-ethylhexyl stearate (Cetiol® 868), cetyl oleate, glycerine tricaprylate, cocoa fatty alcohol caprinate/caprylate (Cetiol® LC), n-butyl stearate, oleyl erucate (Cetiol® J600), isopropyl palmitate (Rilanit® IPP), oleyl oleate (Cetiol®), hexyl laurate (Cetiol® A), di-n-butyl adipate (Cetiol® B), myristyl myristate (Cetiol® MM), cetearyl isononanoate (Cetiol® SN), decyl oleate (Cetiol® V).

- esters of dicarboxylic acids, such as di-n-butyl adipate, di(2-ethylhexyl) adipate, di(2-ethylhexyl) succinate and diisotridecyl acetate, and diol esters, such as ethylene glycol dioleate, ethylene glycol diisotridecanoate, propylene glycol di(2-ethyl hexanoate), propylene glycol diisostearate, propylene glycol dipelargonate, butanediol diisostearate and neopentylglycol dicaprylate,
- symmetrical, unsymmetrical or cyclic esters of carbon dioxide with fatty alcohols, for example glycerine carbonate or dicapryl carbonate (Cetiol® CC), described in DE-OS 197 56 454,
- trifatty acid esters of saturated and/or unsaturated linear and/or branched fatty acids with glycerine,
- partial glycerides of fatty acids, i.e. monoglycerides, diglycerides and their technical mixtures. On use, these technical products can still contain slight

quantities of triglycerides due to the manufacturing process. The partial glycerides preferably have the formulae (D4-I),



(D4-I)

in which R^1, R^2 and R^3 independently of one another represent hydrogen or a linear or branched, saturated and/or unsaturated acyl radical with 6 to 22, preferably 12 to 18 carbon atoms, with the proviso that at least one of these groups represents an acyl radical and at least one of these groups represents hydrogen. The sum (m + n + q) equals 0 or numbers from 1 to 100, preferably 0 or 5 to 25. Preferably R^1 represents an acyl radical and R^2 and R^3 hydrogen and the sum (m + n + q) is 0. Typical examples are mono and/or diglycerides based on caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid as well as their technical mixtures. Preferably, monoglycerides of oleic acid are used.

The quantity added of natural and synthetic cosmetic oils in the inventive formulations normally ranges from 0.1 – 30 wt.%, based on the total composition, preferably 0.1 – 20 wt.%, and especially 0.1 – 15 wt.%.

The total quantity of oil and fat components in the inventive compositions normally ranges from 0.5 – 75 wt.%, based on the total composition. According to the invention, quantities of 0.5 – 35 wt.% are preferred.

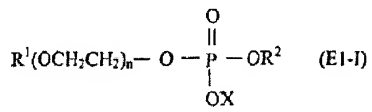
The combination of the active substance complex (A) with surfactants (E) has proved to be particularly advantageous. In a further preferred embodiment, the formulations used according to the invention comprise surfactants. The term surfactant is understood to mean surface-active materials that form adsorbed

layers on surfaces and interfaces or can aggregate in volume phases to micelle colloids or lyotropic mesophases. One differentiates anionic surfactants consisting of a hydrophobic radical and a negatively charged hydrophilic head group, amphoteric surfactants that carry both a negative and also a compensating positive charge, cationic surfactants that beside a hydrophobic radical possess a positive charged hydrophilic group, and non-ionic surfactants that are uncharged but have strong dipole moments and are strongly hydrated in aqueous solution. More detailed definitions and properties of surfactants are to be found in "H.-D. Dörfler, Grenzflächen- und Kolloidchemie, VCH Verlagsgesellschaft mbH. Weinheim, 1994". The above-cited definitions are found from p. 190 in this publication.

Suitable anionic surfactants for the preparations according to the invention are any anionic surface-active substances suitable for use on the human body. Such substances are characterized by a water-solubilizing anionic group such as, for example, a carboxylate, sulfate, sulfonate or phosphate group and a lipophilic alkyl group containing around 8 to 30 carbon atoms. In addition, glycol or polyglycol ether groups, ester, ether, amide and hydroxyl groups may also be present in the molecule. The following are examples of suitable anionic surfactants, each in the form of the sodium, potassium and ammonium salts as well as mono-, di- and trialkanolammonium salts containing 2 to 4 carbon atoms in the alkanol group,

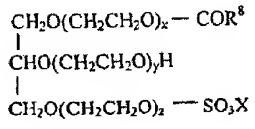
- linear and branched fatty acids containing 8 to 30 carbon atoms (soaps),
- ether carboxylic acids with the formula $R\text{-}O\text{-}(CH_2\text{-}CH_2O)_x\text{-}CH_2\text{-}COOH$, in which R is a linear alkyl group containing 8 to 30 carbon atoms and x = 0 or 1 to 16,
- acyl sarcosides containing 8 to 24 carbon atoms in the acyl group,
- acyl taurides containing 8 to 24 carbon atoms in the acyl group,
- acyl isethionates containing 8 to 24 carbon atoms in the acyl group,
- mono- and dialkyl sulfosuccinates containing 8 to 24 carbon atoms in the alkyl group and monoalkyl polyoxyethyl sulfosuccinates containing 8 to 24 carbon atoms in the alkyl group and 1 to 6 oxyethyl groups.

- linear alkane sulfonates containing 8 to 24 carbon atoms,
- linear alpha-olefin sulfonates containing 8 to 24 carbon atoms,
- methyl esters of alpha-sulfofatty acids from fatty acids containing 8 to 30 carbon atoms,
- alkyl sulfates and alkyl polyglycol ether sulfates corresponding to the formula $R\text{-}O(CH_2\text{-}CH_2O)_x\text{-}OSO_3H$, in which R is a preferably linear alkyl group containing 8 to 30 carbon atoms and x = 0 or 1 to 12,
- mixtures of surface-active hydroxysulfonates according to DE-A-37 25 030,
- sulfated hydroxyalkyl polyethylene- and/or hydroxyalkylene propylene glycol ethers according to DE-A-37 23 354,
- sulfonates of unsaturated fatty acids containing 8 to 24 carbon atoms and 1 to 6 double bonds according to DE-A-39 26 344,
- esters of tartaric acid and citric acid with alcohols in the form of addition products of around 2 to 15 molecules of ethylene oxide and/or propylene oxide with fatty alcohols containing 8 to 22 carbon atoms.
- alkyl and/or alkenyletherphosphates of formula (E1-I),



(E1-I)

- in which R^1 is preferably an aliphatic hydrocarbyl radical containing 8 to 30 carbon atoms, R^2 is hydrogen, a $(CH_2\text{-}CH_2O)_nR^2$ or X, n is a number from 1 to 10 and X is hydrogen, an alkali or alkali earth metal or $NR^3R^4R^5R^6$, with R^3 to R^6 independently of each other representing hydrogen or a C_1 to C_4 hydrocarbyl radical,
- sulfated alkyleneglycol esters of fatty acids of formula (E1-II)
  $R^7CO(AlkO)_nSO_3M$ (E1-II)
  in which R^7CO- is a linear or branched, aliphatic, saturated and/or unsaturated acyl radical with 6 to 22 C atoms, Alk is CH_2CH_2, $CHCH_3CH_2$ and/or CH_2CHCH_3, n is a number from 0.5 to 5 and M is a cation, as described in DE-OS 197 36 906.5,
- monoglyceride sulfates and monoglyceride ether sulfates of formula (E1-III)



(E1-III)

in which R^8CO is a linear or branched acyl radical with 6 to 22 carbon atoms, x, y and z total 0 or are numbers from 1 to 30, preferably 2 to 10, and X is an alkali or earth alkali metal. Typical examples of suitable monoglyceride (ether) sulfates in the sense of the invention are the reaction products of lauric acid monoglyceride, coconut oil acid monoglyceride, palmitic acid monoglyceride, stearic acid monoglyceride, oleic acid monoglyceride and tallow acid monoglyceride as well as their ethylene oxide adducts with sulfur trioxide or chlorosulfonic acid in the form of their sodium salts. Preferably monoglyceride sulfates of formula (E1-III) are used, where R^8CO is a linear or branched acyl radical with 8 to 18 carbon atoms, as described in EP-B1 0 561 825, EP-B1 0 561 999, DE-A1 42 04 700 or by A. K. Biswas et al. in J. Amer. Oil Chem. Soc. 37, 171 (1960) and F. U. Ahmed in J. Amer. Oil Chem. Soc. 67, 8 (1990).

- Amide ether carboxylic acids as described in EP 0 690 044,
- Condensation products of $C_8 - C_{30}$ fatty alcohols with protein hydrolyzates and/or amino acids and their derivatives known to those skilled in the art as albumen fatty acid condensates, as for example Lamepon® types, Gluadin® types, Hostapon® KCG or the Amisoft® types.

Preferred anionic surfactants are alkyl sulfates, alkyl polyglycol ether sulfates and ether carboxylic acids containing 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule and sulfosuccinic acid monoalkylpolyoxyethyl esters with 8 to 18 C atoms in the alkyl group and 1 to 6 oxyethyl groups, monoglyceride sulfates, alkyl- and alkenylether phosphates as well as albumen fatty acid condensates.

Zwitterionic surfactants (E2) are surface-active compounds, which contain at least one quaternary ammonium group and at least one $-COO^{(-)}$ or $-SO_3^{(-)}$ group

in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as N-alkyl-N,N-dimethyl ammonium glycinates, for example cocoalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinates, for example cocoacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and cocoacylaminoethyl hydroxyethyl carboxymethyl glycinate. A preferred zwitterionic surfactant is the fatty acid amide derivative known by the INCI name of Cocamidopropyl Betaine of known fatty acid derivatives.

Ampholytic surfactants (E3) are surface-active compounds which, in addition to a C_8-C_{24} alkyl or acyl group, contain at least one free amino group and at least one -COOH or -SO_3H group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkyl aminobutyric acids, N-alkyl iminodipropionic acids, N-hydroxyethyl-N-alkyl amidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkyl aminopropionic acids and alkyl aminoacetic acids containing around 8 to 24 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkyl amino-propionate, cocoacyl aminoethyl aminopropionate and C_{12}-C_{18} acyl sarcosine.

Nonionic surfactants (E4) contain, for example, a polyol group, a poly-alkylene glycol ether group or a combination of polyol and polyglycol ether groups as the hydrophilic group. Examples of such compounds are

- products of the addition of 2 to 50 mol ethylene oxide and/or 0 to 5 mol propylene oxide onto linear and branched fatty alcohols containing 8 to 30 carbon atoms, onto fatty acids containing 8 to 30 carbon atoms and onto alkylphenols containing 8 to 15 carbon atoms in the alkyl group,
- methyl- or C_2-C_6 alkyl group end-blocked addition products of 2 to 50 mol ethylene oxide and/or 0 to 5 mol propylene oxide onto linear and branched fatty alcohols containing 8 to 30 carbon atoms, onto fatty acids containing 8 to 30 carbon atoms and onto alkylphenols containing 8 to 15 carbon atoms

in the alkyl group, such as for example commercially available types with the trade names Dehydol® LS, Dehydol® LT (Cognis),

- C_{12}-C_{30} fatty acid monoesters and diesters of products of the addition of 1 to 30 mol ethylene oxide onto glycerol,
- products of the addition of 5 to 60 mol ethylene oxide onto castor oil and hydrogenated castor oil,
- polyol esters of fatty acids such as the commercial product Hydagen® HSP (Cognis) or Sovermol types (Cognis),
- alkoxylated triglycerides,
- alkoxylated alkyl esters of fatty acids of formula (E4-I)

$$R^1CO\text{-}(OCH_2CHR^2)_wOR^3 \qquad \text{(E4-I)}$$

in which R^1CO is a linear or branched, saturated and/or unsaturated acyl radical with 6 to 22 carbon atoms, R^2 is hydrogen or methyl, R3 is a linear or branched alkyl radical with 1 to 4 carbon atoms and w is a number from 1 to 20,

- amine oxides
- mixed hydroxyethers as described in DE-OS 197 38 866,
- sorbitan fatty acid esters and products of the addition of ethylene oxide onto sorbitan fatty acid esters such as polysorbates,
- sugar esters of fatty acids and products of the addition of ethylene oxide onto sugar esters of fatty acids
- products of the addition of ethylene oxide onto fatty acid alkanolamides and fatty amines,
- sugar surfactants of the alkyl- and alkenyl oligoglycoside type according to formula (E4-II)

$$R^4O\text{-}[G]_p \qquad \text{(E4-II)}$$

in which R4 is an alkyl or alkenyl radical with 4 to 22 carbon atoms, G is a sugar radical with 5 to 6 carbon atoms and p is a number from 1 to 10. They can be prepared according to relevant methods of organic chemical synthesis. As representatives of the extensive literature, may be cited the review article from Biermann et al. in Starch/Stäarke 45, 281 (1993), B.

Salka in Cosm. Toil. 108, 89 (1993) and J. Kahre et al. in SOFW-Journal 8, 598 (1995).

The alkyl and/or alkenyl oligoglycosides may be derived from aldoses or ketoses containing 5 or 6 carbon atoms, preferably glucose. Accordingly, the preferred alkyl and/or alkenyl oligoglycosides are alkyl and/or alkenyl oligoglucosides. The index p in general formula (E4-II) indicates the degree of oligomerization (DP), i.e. the distribution of mono- and oligoglycosides, and is a number from 1 to 10. Whereas p in a given compound must always be an integer and, above all, may assume a value of 1 to 6, the value p for a given alkyl oligoglycoside is an analytically determined calculated quantity which is generally a fractional number. Alkyl and/or alkenyl oligoglycosides having an average degree of oligomerization p of 1.1 to 3.0 are preferably used. Alkyl and/or alkenyl oligoglycosides having a degree of oligomerization of less than 1.7 and, more particularly, between 1.2 and 1.4 are preferred from the practical point of view. The alkyl or alkenyl radical R^4 may be derived from primary alcohols containing 4 to 11 and preferably 8 to 10 carbon atoms. Typical examples are butanol, caproic alcohol, caprylic alcohol, capric alcohol and undecyl alcohol and the technical mixtures thereof obtained, for example, in the hydrogenation of technical fatty acid methyl esters or in the hydrogenation of aldehydes from Roelen's Oxo synthesis. Alkyl oligoglucosides having a chain length of C_8-C_{10} (DP = 1 to 3), which are obtained as the first runnings in the separation of technical C_8-C_{18} coconut oil fatty alcohol by distillation and which may contain less than 6% by weight of C_{12} alcohol as an impurity, and also alkyl oligoglucosides based on technical $C_{9/11}$ oxoalcohols (DP = 1 to 3) are preferred. In addition, the alkyl or alkenyl radical R^{15} may also be derived from primary alcohols containing 12 to 22, preferably 12 to 14 carbon atoms. Typical examples are lauryl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol, brassidyl alcohol and technical mixtures thereof

which may be obtained as described above. Alkyl oligoglucosides based on hydrogenated $C_{12/14}$ cocoalcohol with a DP of 1 to 3 are preferred.

- Sugar surfactants of the type fatty acid-N-alkylpolyhydroxyalkyl amides, a non-ionic surfactant of formula (E4-III)

$$R^5CO\text{-}NR^6\text{-}[Z] \qquad \text{(E4-III)}$$

in which R^5CO is an aliphatic acyl radical with 6 to 22 carbon atoms, R^6 is hydrogen, an alkyl- or hydroxyalkyl radical with 1 to 4 carbon atoms and [Z] is a linear or branched polyhydroxyalkyl radical with 3 to 12 carbon atoms and 3 to 10 hydroxyl groups. Fatty acid-N-alkylpolyhydroxyalkyl amides are known compounds that can be normally obtained by the reductive amination of a reducing sugar with ammonia, an alkylamine or an alkanolamine followed by acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride. Their synthesis process is reported in US Patents US 1,985,424, US 2,016,962 and US 2,703,798 as well as the international patent application WO 92/06984. A review of this subject by H. Kelkenberg can be found in Tens. Surf. Det. 25, 8 (1988). Preferably, the fatty acid-N-alkylpolyhydroxyalkyl amides are based on reducing sugars with 5 or 6 carbon atoms, particularly glucose. The preferred fatty acid-N-alkylpolyhydroxyalkyl amides are fatty acid-N-alkylglucamides, as shown in formula (E4-IV):

$$R^7CO\text{-}NR^8\text{-}CH_2\text{-}(CHOH)_4\text{-}CH_2OH \qquad \text{(E4-IV)}$$

Preferably glucamides of formula (E4-IV) are used as the fatty acid-N-alkylpolyhydroxyalkyl amides in which R^8 is hydrogen or an alkyl group and R^7CO is an acyl radical of caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid or their technical mixtures. Fatty acid-N-alkylglucamides as shown in formula (E4-IV) are particularly preferred and obtained by reductive amination of glucose with methylamine and subsequent acylation with lauric acid or C12/14 coco fat acid or a

corresponding derivative. In addition, the polyhydroxyalkyl amides can also be based on maltose and palatinose.

The alkyleneoxide-addition products on saturated linear fatty alcohols and fatty acids with 2 to 30 mole ethylene oxide per mole fatty alcohol or fatty acid have proven to be preferred nonionic surfactants. Preparations with outstanding properties are also obtained if they comprise fatty acid esters of ethoxylated glycerine as the nonionic surfactants.

These compounds are characterized by the following parameters. The alkyl radical R contains 6 to 22 carbon atoms and can be both linear and also branched. Primary linear aliphatic radicals and aliphatic radicals with a methyl branch at the 2-position are preferred. 1-octyl, 1-decyl, 1-lauryl, 1-myristyl, 1-cetyl and 1-stearyl are examples of such aliphatic radicals. 1-octyl, 1-decyl, 1-lauryl and 1-myristyl are particularly preferred. Using so-called "Oxo alcohols as starting materials, compounds with an odd number of carbon atoms in the alkyl chain predominate.

Furthermore, the sugar surfactants are quite particularly preferred nonionic surfactants. The compositions used according to the invention preferably comprise them in quantities of 0.1 - 20 wt.%, based on the total composition. Quantities of 0.5 – 15 wt.% are preferred and quantities of 0.5 – 7.5 wt.% are quite particularly preferred.

The compounds used as surfactants with alkyl groups may be homogeneous compounds. In general, however, these compounds are produced from natural vegetal or animal raw materials and result in mixtures of products with raw material dependent, different alkyl chain lengths.

The surfactants representing addition products of ethylene and/or propylene oxide with fatty alcohols or derivatives of these addition products may be both products with a "normal" homolog distribution and products with a narrow

homolog distribution. Products with a "normal" homolog distribution are mixtures of homologs which are obtained from the reaction of fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alcoholates as catalysts. By contrast, narrow homolog distributions are obtained when, for example, hydrotalcites, alkaline earth metal salts of ether carboxylic acids, alkaline earth metal oxides, hydroxides or alcoholates are used as catalysts. The use of products with a narrow homolog distribution can be preferred.

The surfactants (E) are used in quantities of 0.1 – 45 wt.%, preferably 0.5 – 30 wt.% and quite particularly preferably 0.5 – 25 wt.%, based on the total composition used according to the invention.

According to the invention, cationic surfactants (E5), such as quaternary ammonium compounds, esterquats and amidoamines are also useable. Preferred quaternary ammonium compounds are ammonium halides, particularly chlorides and bromides, such as alkyl trimethyl ammonium chlorides, dialkyl dimethyl ammonium chlorides and trialkyl methyl ammonium chlorides, for example cetyl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, lauryl dimethyl ammonium chloride, lauryl dimethyl benzyl ammonium chloride and tricetyl methyl ammonium chloride as well as imidazolium compounds known under the INCI designations Quaternium-27 and Quaternium-83. The long alkyl chains of the above-cited surfactants preferably contain 10 to 18 carbon atoms.

Esterquats are known compounds, which have both an ester group and at least one quaternary ammonium group in their structure. Preferred esterquats are quaternized ester salts of fatty acids with triethanolamine, quaternized ester salts of fatty acids with diethanolalkylamines, and quaternized ester salts of fatty acids with 1,2-dihydroxypropyldialkylamines. Such products are marketed for example under the trade names Stepantex®, Dehyquart® and Armocare®. The products Armocare® VGH-70, a N,N-bis(2-palmitoyloxyethyl)dimethyl

ammonium chloride, as well as Dehyquart® F-75, Dehyquart® C-4046, Dehyquart® L80 and Dehyquart® AU-35 are examples of such esterquats.

The alkyl amidoamines are usually manufactured by the amidation of natural or synthetic fatty acids and fatty acid fractions with dialkylaminoamines. A particularly suitable compound according to the invention from this group of substances is stearyl amidopropyldimethylamine, commercially available under the trade name Tegoamid® S 18.

The compositions used according to the invention preferably comprise the cationic surfactants (E5) in quantities of 0.05 – 10 wt.%, based on the total composition. Quantities of 0.1 – 5 wt.% are particularly preferred.

Anionic, nonionic, zwitterionic and/or amphoteric surfactants and mixtures thereof can be preferred according to the invention.

In a further preferred embodiment, the effect of the inventive active substance complex (A) can be increased by emulsifiers (F). Emulsifiers bring about the formation of water or oil-stable adsorption layers at the phase boundary layer, which protect the dispersed droplets against coalescence and consequently stabilize the emulsion. Hence, emulsifiers, like surfactants, are made up of a hydrophobic and a hydrophilic part of a molecule. Hydrophilic emulsifiers form preferably O/W emulsions and hydrophobic emulsifiers form preferably W/O emulsions. An emulsion is defined as a dispersion of droplets of a liquid in another liquid by means of an energy input to form stabilized phase boundary layers with surfactants. The choice of the emulsifying surfactant or emulsifier is determined by the materials to be dispersed, the respective external phases and the fineness of dispersion of the emulsion. Further definitions and properties of emulsifiers can be found in "H.-D. Dörfler, Grenzflächen- und Kolloidchemie, VCH Verlagsgesellschaft mbH, Weinheim, 1994". According to the invention, examples of usable emulsifiers are

- addition products of from 4 to 30 mol of ethylene oxide and/or 0 to 5 mol of propylene oxide onto linear fatty alcohols having 8 to 22 carbon atoms, onto fatty acids having 12 to 22 carbon atoms and onto alkylphenols having 8 to 15 carbon atoms in the alkyl group,
- C_{12}-C_{22} fatty acid mono- and diesters of addition products of from 1 to 30 mol of ethylene oxide onto polyols having 3 to 6 carbon atoms, in particular onto glycerol,
- ethylene oxide and polyglycerol addition products onto methyl glucoside fatty acid esters, fatty acid alkanolamides and fatty acid glucamides,
- C_8-C_{22} alkyl mono- and oligoglycosides and ethoxylated analogs thereof, wherein degrees of oligomerization of from 1.1 to 5, in particular 1.2 to 2.0, and glucose as the sugar component are preferred,
- mixtures of alkyl (oligo) glucosides and fatty alcohols, for example the commercially available product Montanov® 68,
- addition products of from 5 to 60 mol of ethylene oxide onto castor oil and hydrogenated castor oil,
- partial esters of polyols having 3-6 carbon atoms with saturated fatty acids having 8 to 22 carbon atoms,
- sterols. Sterols are understood to mean a class of steroids, which have a hydroxyl group on the 3rd carbon atom of the steroid backbone and are isolated from both animal tissue (zoosterols) and from vegetable fats (phytosterols). Examples of zoosterols are cholesterol and lanosterol. Examples of suitable phytosterols are ergosterol, stigmasterol and sitosterol. Also, Sterols isolated from fungi and yeasts are called mycosterols.
- Phospholipids. These are understood to mean primarily the glucose-phospholipids that are obtained, for example, as lecithins or phosphatidyl cholines from egg yolk or plant seeds (e.g. soybeans) for example.
- Fatty acid esters of sugars and sugar alcohols, such as sorbitol,
- polyglycerols and polyglycerol derivatives, such as, for example, polyglycerol poly12-hydroxystearate (commercial product Dehymuls® PGPH),

- linear and branched fatty acids having 8 to 30 carbon atoms and their Na, K, ammonium, Ca, Mg and Zn salts.

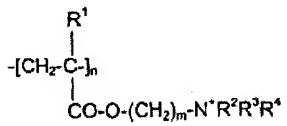
The compositions according to the invention comprise the emulsifiers preferably in amounts of 0.1-25 wt.%, in particular 0.5-15 wt.%, based on the overall composition.

Preferably, the compositions according to the invention can comprise at least one nonionic emulsifier with an HLB value of from 8 to 18, according to the definitions given in Römpp Lexikon Chemie (Ed. J. Falbe, M. Regitz), 10th edition, Georg Thieme Verlag Stuttgart, New York, (1997), page 1764. According to the invention nonionogenic emulsifiers with a HLB value of 10-15 may be particularly preferred.

Further advantageously it has been found that polymers (G) can support the effect of the inventive active substance complex (A). In a preferred embodiment, polymers are therefore added to the compositions used according to the invention, cationic, anionic, amphoteric and also nonionic polymers having proved to be particularly effective.

Cationic polymers (G1) are understood to mean polymers, which have a group that may be "temporarily" or "permanently" cationic in the backbone and/or side chain. According to the invention, "permanently cationic" is used to refer to those polymers that comprise a cationic group independently of the pH of the composition. These are usually polymers that comprise a quaternary nitrogen atom, for example in the form of an ammonium group. Preferred cationic groups are quaternary ammonium groups. In particular, those polymers in which the quaternary ammonium groups are bonded via a C1-4-hydrocarbon group to a polymer backbone constructed from acrylic acid, methacrylic acid or their derivatives have proven particularly suitable.

Homopolymers of the general formula (G1-1),



(G1-I)

in which R^1 = -H or $-CH_3$, R^2, R^3 and R^4, independently of one another, are chosen from C1-4-alkyl, -alkenyl or -hydroxyalkyl groups, m = 1, 2, 3 or 4, n is a natural number and X^- is a physiologically compatible organic or inorganic anion, as well as copolymers consisting essentially of the monomer units listed in formula (G1-I), and also nonionogenic monomer units are particularly preferred cationic polymers. Within the scope of these polymers, preference is given according to the invention to those for which at least one of the following conditions applies:

R^1 is a methyl group
R^2, R^3 and R^4 are methyl groups
m has the value 2.

Suitable physiologically compatible counter ions X^- are, for example, halide ions, sulfate ions, phosphate ions, methosulfate ions, and organic ions, such as lactate-, citrate-, tartrate- and acetate ions. Preference is given to halide ions, in particular chloride.

A particularly suitable homopolymer is the, if desired crosslinked, poly(methacryloyloxyethyltrimethylammonium chloride) with the INCI name Polyquaternium-37. The crosslinking can be carried out, if desired using polyunsaturated olefinic compounds, for example divinylbenzene, tetraallyloxyethane, methylenebisacrylamide, diallyl ether, polyallyl polyglyceryl ether, or allyl ethers of sugars or sugar derivatives, such as erythritol, pentaerythritol, arabitol, mannitol, sorbitol, sucrose or glucose. Methylenebisacrylamide is a preferred crosslinking agent.

The homopolymer is preferably used in the form of a non-aqueous polymer dispersion, which should have a polymer content of not less than 30 wt.%. Such

polymer dispersions are commercially available under the names Salcare® SC 95 (about 50% polymer content, further components: Mineral Oil (INCI name) and tridecylpolyoxypropylene polyoxyethylene ether (INCI name: PPG-1 Trideceth-6)) and Salcare® SC 96 (about 50% polymer content, further components: mixture of diesters of propylene glycol with a mixture of caprylic and capric acid (INCI name: Propylene Glycol Dicaprylate/Dicaprate) and tridecylpolyoxypropylene polyoxyethylene ether (INCI name: PPG-1 Trideceth-6)).

Copolymers with monomer units according to formula (G1-I) contain, as nonionogenic monomer units, preferably acrylamide, methacrylamide, C_{1-4}-alkyl acrylates and C_{1-4}-alkyl methacrylates. Of these nonionogenic monomers, the acrylamide is particularly preferred. As described above for the case of the homopolymers, these copolymers may also be crosslinked. Crosslinked acrylamide-methacryloyloxyethyltrimethylammonium chloride copolymer is a preferred copolymer according to the invention. Those copolymers in which the monomers are present in a weight ratio of about 20:80, are available commercially as ca. 50% concentrated non-aqueous polymer dispersion under the name Salcare® SC 92.

Further preferred cationic polymers are, for example,

- quaternized cellulose derivatives, as are available commercially under the names Celquat® and Polymer JR®. The compounds Celquat® H 100, Celquat® L 200 and Polymer JR® 400 are preferred quaternized cellulose derivatives,
- cationic alkyl polyglycosides according to German patent DE 44 13 686,
- cationized honey, for example the commercial product Honeyquat® 50,
- cationic guar derivatives, such as, in particular, the products sold under the trade names Cosmedia® Guar and Jaguar®,
- polysiloxanes with quaternary groups, such as, for example, the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethylsilylamodimethicone), Dow Corning® 929 Emulsion

(comprising a hydroxylamino-modified silicone, which is also referred to as Amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethylsiloxanes, Quaternium-80),

- polymers of dimethyldiallylammonium salts and copolymers thereof with esters and amides of acrylic acid and methacrylic acid. The products available commercially under the names Merquat® 100 (poly(dimethyldiallylammonium chloride)) and Merquat® 550 (dimethyldiallylammonium chloride-acrylamide copolymer) are examples of such cationic polymers,
- copolymers of vinyl pyrrolidone with quaternized derivatives of the dialkylaminoalkyl acrylate and methacrylate, such as, for example, vinyl pyrrolidone-dimethylaminoethyl methacrylate copolymers quaternized with diethyl sulfate. Such compounds are available commercially under the names Gafquat® 734 and Gafquat® 755,
- vinyl pyrrolidone-vinyl imidazolium methochloride copolymers, as offered under the names Luviquat® FC 370, FC 550, FC 905 and HM 552,
- quaternized polyvinyl alcohol,
- and the polymers with quaternary nitrogen atoms in the polymer backbone known under the names Polyquaternium 2, Polyquaternium 17, Polyquaternium 18 and Polyquaternium 27.

It is likewise possible to use the polymers known under the names Polyquaternium-24 (commercial product e.g. Quatrisoft® LM 200) as cationic polymers. According to the invention, it is likewise possible to use the copolymers of vinyl pyrrolidone, as are available as commercial products Copolymer 845 (manufacturer: ISP), Gaffix® VC 713 (manufacturer: ISP), Gafquat® ASCP 1011, Gafquat® HS 110, Luviquat® 8155 and Luviquat® MS 370.

Further cationic polymers according to the invention are the so-called "temporarily cationic" polymers. These polymers usually contain an amino

group, which, at certain pH values, is in the form of a quaternary ammonium group and thereby cationic. Preference is given, for example, to chitosan and derivatives thereof, as are freely available commercially, for example, under the trade names Hydagen® CMF, Hydagen® HCMF, Kytamer® PC and Chitolam® NB/101.

Cationic polymers which are preferred according to the invention are cationic cellulose derivatives and chitosan and derivatives thereof, in particular the commercial products Polymer® JR 400, Hydagen® HCMF and Kytamera® PC, cationic guar derivatives, cationic honey derivatives, in particular the commercial product Honeyquat® 50, cationic alkyl polyglycosides according to German patent DE 44 13 686 and polymers of the Polyquaternium-37 type.

In addition, cationized protein hydrolyzates are also a type of cationic polymer, where the parent protein hydrolyzate can originate from the animal, for example from collagen, milk or keratin, from plants, for example from wheat, corn, rice, potatoes, soybean or almonds, from marine life forms, for example from fish collagen or algae, or protein hydrolyzates obtained by biotechnological methods. The cationic derivatives based on protein hydrolyzates according to the invention can be obtained from the corresponding proteins by chemical, in particular alkaline or acidic hydrolysis, by enzymatic hydrolysis and/or a combination of the two types of hydrolysis. Hydrolysis of proteins usually affords a protein hydrolyzate with a molecular weight distribution of about 100 Daltons up to several thousand Daltons. Preference is given to those cationic protein hydrolyzates whose parent protein content has a molecular weight of from 100 up to 25,000 Daltons, preferably 250 to 5000 Daltons. In addition, cationic protein hydrolyzates are understood to mean quaternized amino acids and mixtures thereof. Quaternization of the protein hydrolyzates or of the amino acids is often carried out using quaternary ammonium salts, such as, for example, N,N-dimethyl-N-(n-alkyl)-N-(2-hydroxy-3-chloro-n-propyl)ammonium halides. In addition, the cationic protein hydrolyzates can also be derivatized still further. Typical examples of the cationic protein hydrolyzates and derivatives

according to the invention which may be mentioned are the products given under the INCI names in the "International Cosmetic Ingredient Dictionary and Handbook" (seventh edition 1997, The Cosmetic, Toiletry and Fragrance Association 1101 17th Street, N.W., Suite 300, Washington, D.C. 20036-4702) and commercially available: Cocodimonium Hydroxypropyl Hydrolyzed Collagen, Cocodimopnium Hydroxypropyl Hydrolyzed Casein, Cocodimonium Hydroxyprcpyl Hydrolyzed Collagen, Cocodimonium Hydroxypropyl Hydrolyzed Hair Keratin, Cocodimonium Hydroxypropyl Hydrolyzed Keratin, Cocodimonium Hydroxypropyl Hydrolyzed Rice Protein, Cocodimonium Hydroxypropyl Hydrolyzed Silk, Cocodimonium Hydroxypropyl Hydrolyzed Soy Protein, Cocodimonium Hydroxypropyl Hydrolyzed Wheat Protein, Cocodimonium Hydroxypropyl Silk Amino Acids, Hydroxypropyl Arginine Lauryl/Myristyl Ether HCl, Hydroxypropyltrimonium Gelatin, Hydroxypropyltrimonium Hydrolyzed Casein, Hydroxypropyltrimonium Hydrolyzed Collagen, Hydroxypropyltrimonium Hydrolyzed Conchiolin Protein, Hydroxypropyltrimonium Hydrolyzed keratin, Hydroxypropyltrimonium Hydrolyzed Rice Bran Protein, Hydroxyproypltrimonium Hydrolyzed Silk, Hydroxypropyltrimonium Hydrolyzed Soy Protein, Hydroxypropyl Hydrolyzed Vegetable Protein, Hydroxypropyltrimonium Hydrolyzed Wheat Protein, Hydroxypropyltrimonium Hydrolyzed Wheat Protein/Siloxysilicate, Laurdimonium Hydroxypropyl Hydrolyzed Soy Protein, Laurdimonium Hydroxypropyl Hydrolyzed Wheat Protein, Laurdimonium Hydroxypropyl Hydrolyzed Wheat Protein/Siloxysilicate, Lauryldimonium Hydroxypropyl Hydrolyzed Casein, Lauryldimonium Hydroxypropyl Hydrolyzed Collagen, Lauryldimonium Hydroxypropyl Hydrolyzed Keratin, Lauryldimonium Hydroxypropyl Hydrolyzed Silk, Lauryldimonium Hydroxypropyl Hydrolyzed Soy Protein, Steardimonium Hydroxypropyl Hydrolyzed Casein, Steardimonium Hydroxypropyl Hydrolyzed Collagen, Steardimonium Hydroxypropyl Hydrolyzed Keratin, Steardimonium Hydroxypropyl Hydrolyzed Rice Protein, Steardimonium Hydroxypropyl Hydrolyzed Silk, Steardimonium Hydroxypropyl Hydrolyzed Soy Protein, Steardimonium Hydroxypropyl Hydrolyzed Vegetable Protein, Steardimonium Hydroxypropyl Hydrolyzed Wheat Protein, Steartrimonium Hydroxyethyl

Hydrolyzed Collagen, Quaternium-76 Hydrolyzed Collagen, Quaternium-79 Hydrolyzed Collagen, Quaternium-79 Hydrolyzed Keratin, Quaternium-79 Hydrolyzed Milk Protein, Quaternium-79 Hydrolyzed Silk, Quaternium-79 Hydrolyzed Soy Protein, Quaternium-79 Hydrolyzed Wheat Protein.

The vegetal based cationic protein hydrolyzates and derivatives are quite particularly preferred.

The anionic polymers (G2) which can support the effect of the inventive active substance complex (A) are anionic polymers that comprise carboxylate and/or sulfonate groups. Examples of anionic monomers of which such polymers can consist are acrylic acid, methacrylic acid, crotonic acid, maleic anhydride and 2-acrylamido-2-methylpropanesulfonic acid. Here, the acidic groups may be completely or partially present as the sodium, potassium, ammonium, mono- or triethanolammonium salt. Preferred monomers are 2-acrylamido-2-methylpropanesulfonic acid and acrylic acid.

Anionic polymers which have proven quite particularly effective are those which contain, as the sole monomer or comonomer, 2-acrylamido-2-methylpropanesulfonic acid, where the sulfonic acid group can completely or partially be in the form of the sodium, potassium, ammonium, mono- or triethanolammonium salt.

The homopolymer of 2-acrylamido-2-methylpropanesulfonic acid, which is commercially available, for example, under the name Rheothik® 11-80 is particularly preferred.

Within this embodiment, it may be preferred to use copolymers of at least one anionic monomer and at least one nonionogenic monomer. With regard to the anionic monomers, reference is made to the substances listed above. Preferred nonionogenic monomers are acrylamide, methacrylamide, acrylic esters, methacrylic esters, vinyl pyrrolidone, vinyl ethers and vinyl esters.

Preferred anionic copolymers are acrylic acid-acrylamide copolymers and, in particular, polyacrylamide copolymers with monomers containing sulfonic acid groups. A particularly preferred anionic copolymer consists of 70 to 55 mol % of acrylamide and 30 to 45 mol % of 2-acrylamido-2-methylpropanesulfonic acid, where the sulfonic acid group is completely or partially in the form of the sodium, potassium, ammonium, mono- or triethanolammonium salt. This copolymer can also be in crosslinked form, where the crosslinking agents used are preferably polyunsaturated olefinic compounds such as tetraallyloxyethane, allylsucrose, allylpentaerythritol and methylenebisacrylamide. Such a polymer is present in the commercial product Sepigel® 305 from SEPPIC. Use of this compound, which as well as comprising the polymer component, comprises a hydrocarbon mixture (C_{13}-C_{14}-isoparaffin) and a nonionogenic emulsifier (Laureth-7), has proven particularly advantageous within the scope of the teaching according to the invention.

The sodium acryloyl-dimethyltaurate copolymers sold under the name Simulgel® 600 as a compound with isohexadecane and polysorbate-80 have also proven particularly effective according to the invention.

Likewise preferred anionic homopolymers are uncrosslinked and crosslinked polyacrylic acids. Here, allyl ethers of pentaerythritol, of sucrose and of propylene may be preferred crosslinking agents. Such compounds are commercially available, for example, under the trade name Carbopol®.

Copolymers of maleic anhydride and methyl vinyl ether, in particular those with crosslinks, are likewise color-retaining polymers. A maleic acid-methyl vinyl ether copolymer crosslinked with 1,9-decadiene is commercially available under the name Stabileze® QM.

Further polymers that can be used to increase the effect of the inventive active substituent complex (A) are amphoteric polymers (G3). The term amphoteric

polymers covers both those polymers that have both free amino groups and free -COOH or SO_3H groups in the molecule and that are capable of forming internal salts, and zwitterionic polymers that contain quaternary ammonium groups and $-COO^-$ or $-SO_3^-$ groups in the molecule, and those polymers which contain -COOH or SO_3H groups and quaternary ammonium groups.

One example of an amphopolymer which can be used according to the invention is the acrylic resin obtainable under the name Amphomer®, which represents a copolymer of tert-butylaminoethyl methacrylate, N-(1,1,3,3-tetramethylbutyl)acrylamide as well as two or more monomers from the group acrylic acid, methacrylic acid and their simple esters.

Further amphoteric polymers which can be used according to the invention are the compounds given in British laid-open specification 2 104 091, European laid-open specification 47 714, European laid-open specification 217 274, European laid-open specification 283 817 and German laid-open specification 28 17 369.

Amphoteric polymers, which can preferably be used are those polymers that are composed essentially of

(a) monomers with quaternary ammonium groups of the general formula (G3-I),

$$R^1\text{-}CH{=}CR^2\text{-}CO\text{-}Z\text{-}(C_nH_{2n})\text{-}N^{(+)}R^3R^4R^5\ A^{(-)} \quad \text{(G3-I)}$$

in which R^1 and R^2, independently of one another, are hydrogen or a methyl group, and R^3, R^4 and R^5, independently of one another, are alkyl groups having 1 to 4 carbon atoms, Z is an NH group or an oxygen atom, n is an whole number from 2 to 5 and $A^{(-)}$ is the anion of an organic or inorganic acid and

(b) monomeric carboxylic acids of the general formula (G3-II),

$$R^6\text{-}CH{=}CR^7\text{-}COOH \quad \text{(G3-II)}$$

in which R^6 and R^7, independently of one another, are hydrogen or methyl groups.

These compounds can be used in accordance with the invention either directly or else in salt form, which is obtained by neutralization of the polymers, for example with an alkali metal hydroxide. With regard to the details of the preparation of these polymers, reference is made expressly to the contents of German laid-open specification 39 29 973. Quite particular preference is given to those polymers in which monomers of type (a) are used in which R^3, R^4 and R^5 are methyl groups, Z is an NH group and $A^{(-)}$ is a halide, methoxysulfate or ethoxysulfate ion; acrylamidopropyltrimethylammonium chloride is a particularly preferred monomer (a). The monomer (b) used for said polymers is preferably acrylic acid.

In a further embodiment, the inventive composition can comprise nonionogenic polymers (G4).

Suitable nonionogenic polymers are for example:

- vinyl pyrrolidone/vinyl ester copolymers, as sold, for example, under the trade mark Luviskol® (BASF). Luviskol® VA 64 and Luviskol® VA 73, both vinyl pyrrolidone/vinyl acetate copolymers are also preferred nonionic polymers.
- cellulose ethers, such as hydroxypropylcellulose, hydroxyethylcellulose and methylhydroxypropylcellulose, as sold, for example, under the trade marks Culminal® and Benecel®.
- shellac
- polyvinyl pyrrolidone, as sold for example under the name Luviskol® (BASF).
- Siloxanes. These siloxanes may be either soluble or insoluble in water. Both volatile or non-volatile siloxanes are suitable, wherein the non-volatile siloxanes mean such compounds with a boiling point above 200°C. Preferred siloxanes are polydialkylsiloxanes, such as for example polydimethylsiloxane, polyalkylarylsiloxanes, such as, for example, polyphenylmethylsiloxane, ethoxylated polydialkoxysilanes as well as polyalkyldisiloxanes the comprise amine and/or hydroxyl groups.

- Glycosidic substituted silicones according to EP 0 612 759 B1.

According to the invention it is also possible for the used preparations to comprise a plurality, particularly two different polymers with the same charge and/or one ionic and one amphoteric and/or nonionic polymer.

The polymers (G) are present in the compositions used according to the invention preferably in amounts of from 0.05 to 10 wt.%, based on the overall composition. Amounts of from 0.1 to 5 wt.%, particularly from 0.1 to 3 wt.%, are particularly preferred.

In a further preferred embodiment of the invention, the effect of the active substance complex (A) can be increased by UV-filters (I). The UV-filters used according to the invention are not subject to any particular limitation, as far as their structure and physical properties are concerned. In fact, all UV-filters that are used in the field of cosmetics with an absorption maximum in the UVA region (315 – 400 nm), in the UVB region (280 – 315 nm) or in the UVC region (< 280 nm) are suitable. UV-filters with an absorption maximum in the UVB region, particularly in the region from about 280 to about 300 nm are particularly preferred.
The UV-filters used according to the invention can, for example, be selected from substituted benzophenones, p-aminobenzoates, diphenylacrylates, cinnamates, salicylates, benzimidazoles and o-aminobenzoates.

Examples of UV-filters used according to the invention are 4-amino-benzoic acid, N,N,N-trimethyl-4-(2-oxoborn-3-ylidenemethyl)aniline-methylsulfate, 3,3,5-trimethylcyclohexylsalicylate (homosalate), 2-hydroxy-4-methoxy-benzophenone (Benzophenone-3; Uvinul® M 40, Uvasorb® MET, Neo Heliopan® BB, Eusolex® 4360), 2-phenylbenzimidazol-5-sulfonic acid and their potassium, sodium und triethanolamine salts (phenylbenzimidazole sulfonic acid; Parsol® HS; Neo Heliopan® Hydro), 3,3'-(1,4-phenylenedimethylene)-bis(7,7-dimethyl-2-oxo-bicyclo-[2.2.1]hept-1-yl-methanesulfonic acid) and their

salts, 1-(4-tert.-butylphenyl)-3-(4-methoxyphenyl)propane-1,3-dione (butyl-methoxydibenzoylmethane; Parsol® 1789, Eusolex® 9020), α-(2-oxoborn-3-ylidene)-toluene-4-sulfonic acid and salts thereof, ethoxylated ethyl 4-aminobenzoate (PEG-25 PABA; Uvinul® P 25), 2-ethylhexyl 4-dimethylaminobenzoate (Octyl Dimethyl PABA; Uvasorb® DMO, Escalol® 507, Eusolex® 6007), 2-ethylhexyl salicylate (Octyl Salicylate; Escalol® 587, Neo Heliopan® OS, Uvinul® O18), isopentyl 4-methoxycinnamate (Isoamyl p-methoxycinnamate; Neo Heliopan® E 1000), 2-ethylhexyl 4-methoxycinnamate (Octyl Methoxycinnamate; Parsol® MCX, Escalol® 557, Neo Heliopan® AV), 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid and sodium salts thereof, (benzophenone-4; Uvinul® MS 40; Uvasorb® S 5), 3-(4'-methylbenzylidene)-D,L-camphor (4-Methylbenzylidene camphor; Parsol® 5000, Eusolex® 6300), 3-benzylidene-camphor (3-Benzylidene camphor), 4-isopropylbenzylsalicylate, 2,4,6-trianilino-(p-carbo-2'-ethylhexyl-1'-oxy)-1,3,5-triazine, 3-imidazol-4-yl-acrylic acid und its ethyl ester, polymers of N (2 and 4)-[2-oxoborn-3-ylidenemethyl]benzyl-acrylamide, 2,4-dihydroxybenzophenone (Benzophenone-1; Uvasorb® 20 H, Uvinul® 400), 2-ethylhexyl ester of 1,1'-diphenylacrylonitrilic acid (Octocrylene; Eusolex® OCR, Neo Heliopan® Type 303, Uvinul® N 539 SG), menthyl o-aminobenzoate (Menthyl Anthranilate; Neo Heliopan® MA), 2,2',4,4'-tetrahydroxybenzophenone (Benzophenone-2, Uvinul® D-50), 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (Benzophenone-6), 2,2'-dihydroxy-4,4'-dimethoxybenzophenone-5-sodium sulfonate und 2'-ethylhexyl 2-cyano-3,3-diphenylacrylate. 4-amino-benzoic acid, N,N,N-trimethyl-4-(2-oxoborn-3-ylidenemethyl)aniline-methylsulfate, 3,3,5-trimethyl-cyclohexylsalicylate, 2-hydroxy-4-methoxy-benzophenone, 2-phenylbenzimidazol-5-sulfonic acid and their potassium, sodium and triethanolamine salts, 3,3'-(1,4-phenylenedimethylene)-bis(7,7-dimethyl-2-oxo-bicyclo-[2.2.1]hept-1-yl-methane-sulfonic acid) and its salts, 1-(4-tert.-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione, α-(2-oxoborn-3-ylidene)-toluene-4-sulfonic acid and its salts, ethoxylated ethyl 4-aminobenzoate, 2-ethylhexyl 4-dimethylaminobenzoate, 2-ethylhexyl salicylate, isopentyl 4-methoxycinnamate, ethylhexyl 4-methoxycinnamate, 2-hydroxy-4-methoxybenzophenone-5-sulfonic

acid und its sodium salt, 3-(4'-methylbenzylidene)-D,L-camphor, 3-benzylidene-camphor, 4-isopropylbenzyl salicylate, 2,4,6-trianilino-(p-carbo-2'-ethylhexyl-1'-oxy)-1,3,5-triazine, 3-imidazol-4-yl-acrylic acid and its ethyl ester, polymers of N-(2 and 4)-[2-oxoborn-3-ylidenemethyl]benzylacrylamide are preferred. According to the invention, 2-hydroxy-4-methoxy-benzophenone, 2-phenylbenzimidazol-5-sulfonic acid and its potassium, sodium and triethanolamine salts, 1-(4-tert.-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione, 2-ethylhexyl 4-methoxycinnamate and 3-(4'-methylbenzylidene)-D,L-camphor are quite particularly preferred.

UV-filters with molar extinction coefficients at the absorption maximum greater than 15000, particularly above 20000 are preferred.

It was further found in the scope of the inventive teaching that for structurally similar UV-filters, in many cases the water-insoluble compound has a higher effect than such water-soluble compounds, which differ from it by one or more additional ionic groups. Within the scope of the invention, water-insoluble means such UV-filters that have a solubility in water at 20°C of not more than 1 wt.%, particularly not more than 0.1 wt.%. In addition, these compounds should have a solubility in typical cosmetic oil components at room temperature of at least 0.1 wt.%, particularly at least 1 wt.%). Accordingly, the use of water-insoluble UV-filters according to the invention may be preferred.

According to a further embodiment of the invention, preferred UV-filters are those that comprise a cationic group, particularly a quaternary ammonium group.

These UV-filters have the general structure U – Q.

Here, the structural moiety U is a UV radiation-absorbing group. In principal, this group stems from the known UV-filters cited above that are used in the field of

cosmetics, in which one group - usually a hydrogen atom – of the UV-filter is replaced by a cationic group Q, particularly by a quaternary amino function.
The structural moiety U can stem from compounds such as, for example,

- substituted benzophenones,
- p-aminobenzoates
- diphenylacrylates
- cinnamates
- salicylates
- benzimidazoles and
- o-aminobenzoates.

According to the invention, structural moieties U, which stem from cinnamides or from N,N-dimethylaminobenzamide are preferred.

In principle, the structural moieties U can be selected so that the absorption maximum of the UV-filter can lie both in the UVA(315-400 nm) and also in the UVB(280-315 nm) or in the UVC(<280 nm) regions. UV-filters with an absorption maximum in the UVB region, particularly from about 280 to about 300 nm are particularly preferred.

In addition, the preferred structural moiety U, which also depends on the structural moiety Q, is chosen such that the molar extinction coefficient of the UV-filter at the absorption maximum lies above 15000, particularly above 20000.

The structural moiety Q preferably comprises a quaternary ammonium group as the cationic group. In principle, this quaternary ammonium group can be directly bonded to the structural moiety U, such that the structural moiety U forms one of the four substituents of the positively charged nitrogen atom. However, one of the four substituents on the positively charged nitrogen atom is preferably a group, particularly an alkylene group of 2 to 6 carbon atoms, which acts as a

spacer between the structural moiety U and the positively charged nitrogen atom.

Advantageously, the group Q has the general structure $-(CH_2)_x-N^+R^1R^2R^3\ X^-$, wherein x is a whole number from 1 to 4, R^1 and R^2 independently of one another are C_{1-4} alkyl groups, R^3 is a C_{1-22} alkyl group or a benzyl group and X^- is a physiologically compatible anion. In the context of this general structure, x is preferably the number 3, R^1 and R^2 are each a methyl group and R^3 is either a methyl group or a saturated or unsaturated, linear or branched hydrocarbon chain with 8 to 22, particularly 10 to 18 carbon atoms.

Exemplary physiologically compatible anions are inorganic anions such as halides, particularly chloride, bromide and fluoride, sulfate ions and phosphate ions as well as organic anions such as lactate, citrate, acetate, tartrate, methosulfate and tosylate.

Two preferred UV-filters with cationic groups are the commercially available products cinnamidopropyl trimethylammonium chloride (Incroquat® UV-283) and dodecyl dimethylaminobenzamidopropyl dimethylammonium tosylate (Escalol® HP 610).

Of course the teaching of the invention also includes the use of a combination of a plurality of UV-filters. In the context of this embodiment, the combination of at least one water-insoluble UV-filter with at least one UV-filter with a cationic group is preferred.

The compositions used according to the invention usually comprise the UV-filters (I) in amounts of 0.1 – 5 wt.% based on the total composition. Amounts of 0.4 – 2.5 wt.% are preferred.

Furthermore, the effect of the inventive active substance complex (A) can be increased by means of a 2-pyrrolidinone-5-carboxylic acid and its derivatives

(J). Accordingly, a further subject of the invention is the use of the active substance in combination with derivatives of 2-pyrrolidinone-5-carboxylic acid. The sodium, potassium, calcium, magnesium or ammonium salts, wherein the ammonium ion is substituted with one to three C_1 to C_4 alkyl groups beside hydrogen are preferred. The sodium salt is quite particularly preferred. The amounts added to the inventive compositions range from 0.05 to 10 wt.% based on the total composition, particularly preferred 0.1 to 5 and especially 0.1 to 3 wt.%.

Also, the combination of the active substance complex (A) with vitamins, provitamins and vitamin precursors as well as their derivatives (K) has proved to be advantageous.

According to the invention, those vitamins, provitamins and vitamin precursors, which are usually classified in the groups A, B, C, E, F and H, are preferred.

In the group of substances designated as vitamin A belong retinol (vitamin A_1) as well as 3,4-didehydroretinol (vitamin A_2). β-carotene is the provitamin of retinol. Examples of suitable vitamin A components according to the invention are vitamin A acid and its esters, vitamin A aldehyde and vitamin A alcohol as well as its esters such as the palmitate and acetate. The preparations used according to the invention comprise the vitamin A components in amounts of 0.05 – 1 wt.% based on the total preparation.

The vitamin B group or the vitamin B complex include among other things

- Vitamin B_1 (Thiamine)
- Vitamin B_2 (Riboflavine)
- Vitamin B_3. The compounds nicotinic acid and nicotinamide are often included under this designation. According to the invention, nicotinamide is preferred and is comprised in the compositions according to the invention in amounts of 0.05 to 1 wt.% based on the total composition.

- Vitamin B_5 (pantothenic acid, panthenol and pantolactone). In the context of this group, panthenol and/or pantolactone are preferably used. Useable derivatives of panthenol according to the invention are especially the esters and ethers of panthenol as well as cationic derivatized panthenols. Specific representatives are for example, panthenol triacetate, panthenol monoethyl ether and its monoacetate as well as the cationic panthenol derivatives disclosed in WO 92/13829. The cited compounds of the vitamin B_5 type are comprised in the compositions used according to the invention in amounts of 0.005 – 10 wt.%, based on the total composition. Amounts of 0.1 – 5 wt.% are particularly preferred.
- Vitamin B_6 (pyridoxine as well as pyridoxamine and pyridoxal).

Vitamin C (ascorbic acid). Vitamin C is preferably added to the compositions used according to the invention in amounts of 0.1 to 3 wt.%, based on the total composition. Its use in the form of the palmitate, the glucoside or phosphate can be preferred. Its use in combination with tocopherols can also be preferred.

Vitamin E (Tocopherols, especially α-tocopherol). Tocopherol and its derivatives, among which particularly the esters such as the acetate, the nicotinate, the phosphate and the succinate, are used in the compositions according to the invention preferably comprised in amounts of 0.05 – 1 wt.%, based on the total composition.

Vitamin F. The term "vitamin F" is usually taken to mean essential fatty acids, particularly linoleic acid, linolenic acid and arachidonic acid.

Vitamin H. The compound (3a*S*,4*S*, 6a*R*)-2-oxchexahydrothienol[3,4-*d*]-imidazol-4.valeric acid denotes Vitamin H, for which the trivial name biotin has become accepted. The compositions according to the invention preferably comprise biotin in amounts of 0.0001 to 1.0 wt.%, particularly in amounts of 0.001 to 0.01 wt.%.

The compositions used according to the invention preferably comprise vitamins, provitamins and vitamin precursors from groups A, B, E and H.

Panthenol, pantolactone, pyridoxine and its derivatives as well as nicotinamide and biotin are particularly preferred.

Finally, the effect of the active substance complex (A) can also be increased by the addition of plant extracts (L).

These extracts are normally prepared by extraction of the whole plant. However, it may be preferred in specific cases to prepare the extracts exclusively from blossoms and/or leaves of the plant.

With regard to the plant extracts suitable for use in accordance with the invention, particular reference is made to the extracts listed in the Table beginning on page 44 of the 3rd Edition of the Leitfadens zur Inhaltsstoffdeklaration kosmetischer Mittel, published by the Industrieverband Körperpflege-und Waschmittel e.V. (IKW), Frankfurt.

According to the invention, above all the extracts of green tea, oak bark, stinging nettle, hamamelis, hops, camomile, burdock root, horse willow, hawthorn, lime blossom, almond, aloe vera, pine needle, horse chestnut, sandalwood, juniper, coconut, mango, apricot, lemon, wheat, kiwi, melon, orange, grapefruit, sage, rosemary, birch, mallow, lady's smock, creeping thyme, yarrow, thyme, balm, restharrow, coltsfoot, hibiscus, meristem, ginseng and ginger root are preferred.

Particularly preferred extracts are those of green tea, oak bark, stinging nettle, hamamelis, hops, camomile, burdock root, horse willow, lime blossom, almond, aloe vera, coconut, mango, apricot, lemon, wheat, kiwi, melon, orange, grapefruit, sage, rosemary, birch, lady's smock, creeping thyme, yarrow, restharrow, meristem, ginseng and ginger root.

Extracts of green tea, almond, aloe vera, coconut, mango, apricot, lemon, wheat, kiwi and melon are quite particularly suitable for the preparations according to the invention.

Extractants suitable for the preparation of the plant extracts mentioned include water, alcohols and mixtures thereof. Among the alcohols, lower alcohols, such as ethanol and isopropanol, but especially polyhydric alcohols, such as ethylene glycol and propylene glycol, both as sole extractants and in admixture with water, are preferred. Plant extracts based on water/propylene glycol in a ratio of 1:10 to 10:1 have proved to be particularly suitable.

According to the invention, the plant extracts may be used both in pure form and in dilute form. If they are used in dilute form, they normally contain ca. 2 – 80 wt.% active substance and - as solvent - the extractant or mixture of extractants used in their preparation.

Furthermore, it can be preferred that mixtures of several, more particularly two different plant extracts are used in the preparations according to the invention.

In addition, it can prove advantageous if besides the inventive active substance complex (A), there are comprised penetration and/or swelling substances (M), such as urea and urea derivatives, guanidine and its derivatives, arginine and its derivatives, water glass, imidazol and its derivatives, histidine and its derivatives, benzyl alcohol, glycerol, glycol and glycol ethers, propylene glycol and propylene glycol ethers, for example propylene glycol monoethyl ether, carbonates, hydrogencarbonates, diols and triols, and particularly 1,2-diols and 1,3-diols such as 1,2-propanediol, 1,2-pentanediol, 1,2-hexanediol, 1,2-dodecanediol, 1,3-propanediol, 1,6-hexanediol, 1,5-pentanediol, 1,4-butanediol.

Advantageously in the context of the invention, short-chain carboxylic acids (N) can additionally support the active substance complex (A). In the context of the

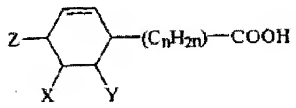
invention, by short-chain carboxylic acids and their derivatives are meant carboxylic acids that can be saturated or unsaturated and/or linear or branched or cyclic and/or aromatic and/or heterocyclic having a molecular weight less than 750. In the context of the invention, saturated or unsaturated linear or branched carboxylic acids with a chain length from 1 to 16 C-atoms are preferred and those with a chain length of 1 to 12 C-atoms are quite particularly preferred.

In the context of the invention, the short-chain carboxylic acids may comprise one, two, three or more carboxyl groups. In the context of the invention, carboxylic acids with a plurality of carboxyl groups are preferred, particularly di- and tricarboxylic acids. The carboxyl groups may be entirely or partially present as ester, acid anhydride, lactone, amide, imido acid, lactam, lactim, dicarboximide, carbohydrazide, hydrazone, hydroxamic, hydroximic, amidine, amidoximic, nitrile, phosphonic or phosphate esters. Of course, the inventive carboxylic acids may be substituted along the carbon chain or the cyclic structure. The substituents of the inventive carboxylic acids are for example C_1-C_8 alkyl, C_2-C_8 alkenyl, aryl, aralkyl and aralkenyl, hydroxymethyl, C_2-C_8 hydroxyalkyl, C_2-C_8 hydroxyalkenyl, aminomethyl, C_2-C_8 aminoalkyl, cyano, formyl, oxo, thioxo, hydroxy, mercapto, amino, carboxy or imino groups. C_2-C_8 alkyl, hydroxymethyl, hydroxy, amino and carboxy groups are preferred. Substituents in the α-position are particularly preferred. Hydroxy, alkoxy and amino groups, wherein the amino function can be optionally further substituted by alkyl, aryl, aralkyl and/or alkenyl radicals, are quite particularly preferred substituents. Further likewise preferred carboxylic acid derivatives are the phosphonic and phosphate esters.

Exemplary inventive carboxylic acids are formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, pivalic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, glycerinic acid, glyoxylic acid, adipic acid, pimelic acid, suberic acid, azelainic acid, sebacic acid, propiolic acid, crotonic acid, isocrotonic acid, elaidic acid, maleic acid, fumaric acid, muconic

acid, citraconic acid, mesaconic acid, camphoric acid, benzoic acid, o, m, p-phthalic acid, naphthoic acid, toluoylic acid, hydratropic acid, atropic acid, cinnamic acid, isonicotinic acid, nicotinic acid, bicarbaminic acid, 4,4'-dicyano-6, 6'-binicotinic acid, 8-carbamoyloctanoic acid, 1,2,4-pentanetricarboxylic acid, 2-pyrrolcarboxylic acid, 1,2,4,6,7-napthalenepentaacetic acid, malonaldehydic acid, 4-hydroxy-phthalamidic acid, 1-pyrazolcarboxylic acid, gallic acid or propanetricarboxylic acid, a dicarboxylic acid selected from the group of compounds of the general formula (N-1),

(N-I)



wherein Z is a linear or branched alkyl or alkenyl group with 4 to 12 carbon atoms, n is a number from 4 to 12 and one of the groups X and Y is a COOH group and the other is hydrogen or a methyl or ethyl radical, dicarboxylic acids of the general formula (N-I) that are additionally substituted with 1 to 3 methyl or ethyl substituents on the cyclohexene ring, as well as dicarboxylic acids according to formula (N-I) formed by the addition of a molecule of water onto the double bond of the cyclohexene ring.

Dicarboxylic acids of the formula (N-I) are known from the literature.

A production process is taken from US Patent 3,753,968 for example. German Patent 22 50 055 discloses the use of these dicarboxylic acids in liquid soaps. Deodorants, which comprise the zinc or the magnesium salts of these dicarboxylic acids, are known from DE-OS-28 33 291. Finally, hair washing and rinsing compositions are known from DE-OS-35 03 618, in which the addition of these dicarboxylic acids provided a markedly improved hair cosmetic effect to the composition that contained water-soluble ionic polymers. Finally, hair treatment compositions, which exhibit effects in terms of care are known from DE-OS-197 54 053.

The dicarboxylic acids of formula (N-I) can for example be synthesized by the reaction of poly-unsaturated dicarboxylic acids with unsaturated monocarboxylic acids according to a Diels-Alder cyclization. Usually, the dicarboxylic acid starting material is a poly-unsaturated fatty acid. Linoleic acid, obtained from natural fatty acids and oils is preferred. The preferred monocarboxylic acid component is particularly acrylic acid, but also methacrylic acid and crotonic acid, for example. Normally, Diels-Alder reactions produce mixtures of isomers in which one component is in excess. According to the invention, this mixture of isomers, as well as the pure compounds may be used.

According to the invention, besides the preferred dicarboxylic acids according to formula (N-I), those dicarboxylic acids that differ from dicarboxylic acids of the general formula (N-I) in that they are substituted with 1 to 3 methyl or ethyl substituents on the cyclohexyl ring or reaction products of these compounds by the formal addition of a molecule of water onto the double bond of the cyclohexene ring are also suitable.

According to the invention, the dicarboxylic acid (mixture) resulting from the reaction of linoleic acid with acrylic acid has proved to be particularly effective. It consists of a mixture of 5- and 6-carboxy-4-hexyl-2-cyclohexene-1-octanoic acid. Such compounds are commercially available under the designations Westvaco Diacid® 1550 and Westvaco Diacid® 1595 (Manufacturer: Westvaco).

Besides the examples of the inventive short-chain carboxylic acids *per se*, cited above, their physiologically compatible salts may also be used according to the invention. Examples of such salts are the alkali, earth alkali, zinc as well as ammonium salts, under which are also meant, in the context of the present application, the mono-, di-, trimethyl-, ethyl- and hydroxyethyl ammonium salts. In the context of the invention, the use of acids, neutralized however with alkali reactive amino acids, for example arginine, lysine, ornithine and histidine may

be quite particularly preferred. Further, for reasons of formulation, it may be preferred to select water-soluble carboxylic acids, particularly the water-soluble salts.

According to the invention it is further preferred to use hydroxycarboxylic acids and here again particularly the dihydroxy, trihydroxy and polyhydroxycarboxylic acids as well as the dihydroxy, trihydroxy and polyhydroxy di-, tri- and polycarboxylic acids with the active substance complex (A). In this regard, it has been shown that besides the hydroxycarboxylic acids, also hydroxycarboxylic acid esters and mixtures of hydroxycarboxylic acids and their esters and also polymeric hydroxycarboxylic acids and their esters may be quite particularly preferred. Preferred hydroxycarboxylic acid esters are for example totally esterified glycolic acid, lactic acid, malic acid, tartaric acid or citric acid. Further fundamentally suitable hydroxycarboxylic acid esters are esters of β-hydroxypropionic acid, tartronic acid, D-gluconic acid, saccharic acid, mucic acid or glucoronic acid. Suitable alcohol components of these esters are primary, linear or branched aliphatic alcohols with 8 – 22 carbon atoms, i.e. fatty alcohols or synthetic fatty alcohols. In this regard, esters of C_{12}-C_{15} fatty alcohols are particularly preferred. Esters of this type are commercially available e.g. under the trade name Cosmacol® from Enichem, Augusta Industriale. Particularly preferred polyhydroxycarboxylic acids are polylactic acid and polytartaric acid and their esters.

Finally, within the context of the teaching of the invention, further protein hydrolyzates and their derivatives (P) which are not derived from natural silk can, of course, be used in addition to the inventive active substance complex (A). Protein hydrolyzates are mixtures of products that are obtained from the acidic, basic or enzymatic catalyzed degradation of proteins (albumins). According to the invention, the term protein hydrolyzates also means total hydrolyzates as well as individual amino acids and their derivatives as well as mixtures of different amino acids and their derivatives. Furthermore, according to the invention, the term protein hydrolyzates means polymers synthesized

from amino acids and derivatives of amino acids. Examples of such polymers are polyalanine, polyaspargine, polyserine etc. Further examples of compounds used according to the invention are L-alanyl-L-proline, polyglycine, glycyl-L-glutamine or D/L-methionine-S-methyl sulfonium chloride. Naturally, β-amino acids and their derivatives such as β-alanine, anthranilic acid or hippuric acid may also be used according to the invention. The molecular weight of the protein hydrolyzates used according to the invention lies between 75, the molecular weight of glycine, and 200000, preferably the molecular weight ranges between 75 and 50000 and quite particularly preferably 75 to 20000 Daltons.

According to the invention, protein hydrolyzates of vegetal, animal, marine or synthetic origin may be used.

Examples of animal protein hydrolyzates are elastin-, collagen-, keratin- and milk albumin-protein hydrolyzates, which may also be present in the form of salts. Such products are sold for example under the trade names Dehylan® (Cognis), Promois® (Interorgana), Collapuron® (Cognis), Nutrilan® (Cognis), Gelita-Sol® (Deutsche Gelatine Fabriken Stoess & Co.), Lexein® (Inolex) and Kerasol® (Croda).

According to the invention, the use of protein hydrolyzates of vegetal origin e.g. protein hydrolyzates of soya, almonds, peas, potatoes and wheat are preferred. such products are available for example, under the trade names Gluadin® (Cognis), Diamin® (Diamalt), Lexein® (Inolex), Hydrosoy® (Croda), Hydrolupin® (Croda), Hydrotritium® (Croda) and Crotein® (Croda).

Although the use of protein hydrolyzates as such is preferred, amino acid mixtures from elsewhere may be optionally used in their place. The use of derivatives of protein hydrolyzates is also possible, for example in the form of their fatty acid condensation products. Such products are sold for example,

under the designations Lamepon® (Cognis), Lexein® (Inolex), Crolastin® (Croda) or Crotein® (Croda).

Naturally, the teaching of the invention includes all isomeric forms like cis – trans isomers, diastereoisomers and chiral isomers.

According to the invention, it is also possible to use a mixture of a plurality of protein hydrolyzates (P).

The compositions comprise the protein hydrolyzates (P) in concentrations of 0.01 up to 20 wt.%, preferably from 0.05 wt.% to 15 wt.% and quite particularly preferably from 0.05 wt.% up to 5 wt.%.

In principal there are no restrictions with regard to the manner in which the inventive active substance complex is applied to the keratinous fibers, particularly human hair. Suitable presentation forms of these preparations are for example creams, lotions, solutions, waters, emulsions like W/O, O/W, PIT emulsions (named PIT emulsions according to the teaching of phase inversion), micro emulsions, and multiple emulsions, gels, sprays, aerosols and foam aerosols. In principle, the pH of these preparations can be between 2 – 11, preferably between 5 and 11, values of 6 to 10 being particularly preferred. This pH can be adjusted by using practically each acid or base that is applicable for cosmetic purposes. Preferred bases are ammonia, alkali hydroxides, monoethanolamine, triethanolamine as well as N,N,N',N'- tetrakis-(2-hydroxypropyl)ethylenediamine.

No-rinse hair preparations have proved to be effective and therefore can be the preferred embodiments of the teaching according to the invention. According to the invention, by no-rinse are meant such preparations that in the context of the treatment are not rinsed out of the hair with the help of water or an aqueous solution after a period of time of some seconds up to an hour. In fact, the

preparations remain on the hair until the next hair wash, i.e. generally more than 12 hours.

According to a preferred embodiment, these preparations are formulated as deep hair conditioners or hair conditioners. The inventive preparations according to this embodiment may be rinsed out with water or at least a predominantly aqueous agent at the end of this contact time; however, they may, as discussed above, be allowed to remain on the hair. Thereby it can be preferred to administer the inventive preparation on the hair before applying a cleansing agent, a waving agent or other hair treatments. In this case, the inventive preparation serves as structural protection for the subsequent applications.

According to further preferred embodiments, the inventive compositions can be also for example be added as pretreatments or rinses for cleansing agents like shampoos, care preparations like rinses, strengthening compositions like hair strengtheners, foam strengtheners, styling gels and hair-dryer curls, permanent shaping compositions like permanent wave and setting compositions, hair colorants like toners, lighteners and oxidative colorants, as well as especially in the scope of a permanent wave setting or a dyeing process.

The inventive active substance complex (A) can in principal be added thereby directly to the colorant, the waving composition or the setting agent. The application of the active substance complex on the keratinous fiber may also occur in a separate step, either before or at the end of the actual coloration or waving process. The teaching of the invention also includes separate treatments, optionally also days or weeks before or after the hair treatment, for example dyeing or waving. However, the application of the inventive active substance complex can occur after the corresponding hair treatment like coloration or waving, especially in the corresponding hair treatment compositions.

Here, the term coloration procedure includes all processes known to those skilled in the art in which a colorant is applied to optionally wetted hair, is left on the hair, either for a time between a few minutes and about 45 minutes and finally rinsed out with water or a composition containing a surfactant, or is left entirely on the hair. In this context, reference is expressly made to known monographs, e.g. K.H. Schrader, Grundlagen und Rezepturen der Kosmetika, 2nd edition, Hüthig Buch Verlag, Heidelberg, 1989, which give an account of the pertinent knowledge of the expert.

The term waving procedure includes all processes known to those skilled in the art in which a waving composition is applied to optionally wetted hair rolled around a curler, is left on the hair, either for a time between a few minutes and about 45 minutes and finally rinsed out with water or a composition containing a surfactant, or a permanent wave setting is subsequently applied on the hair, either for a time between a few minutes and about 45 minutes and finally rinsed out with water or a composition containing a surfactant. In this context, reference is expressly made to known monographs, e.g. K.H. Schrader, Grundlagen und Rezepturen der Kosmetika, 2nd edition, Hüthig Buch Verlag, Heidelberg, 1989, which give an account of the pertinent knowledge of the expert.

In addition to the compulsory required active substance complex (A) and the other preferred components cited above, these preparations may in principle comprise any other components for such cosmetic preparations that are known to those skilled in the art.

Other active substances, auxiliaries and additives are, for example,

- nonionic polymers such as, for example, vinyl pyrrolidone/vinyl acrylate copolymers, polyvinyl pyrrolidone and vinyl pyrrolidone/vinyl acetate copolymers and polysiloxanes,
- thickeners, such as agar agar, guar gum, alginates, xanthane gum, gum arabic, karaya gum, locust bean flour, linseed gums, dextrans, cellulose

derivatives, for example methyl cellulose, hydroxyalkyl cellulose and carboxymethyl cellulose, starch fractions and derivatives, such as amylose, amylopectin and dextrins, clays such as, for example, bentonite or fully synthetic hydrocolloids such as, for example, polyvinyl alcohol,

- hair-conditioning compounds, such as phospholipids, for example soya lecithin, egg lecithin and kephalins, as well as silicone oils,
- perfume oils, dimethyl isosorbide and cyclodextrins,
- solvents and solubilizers, such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol and diethylene glycol,
- symmetrical and unsymmetrical, linear and branched dialkyl ethers with a total of 12 to 36 carbon atoms, particularly 12 to 24 carbon atoms, such as for example, di-n-octyl ether, di-n-decyl ether, di-n-nonyl ether, di-n-undecyl ether and di-n-dodecyl ether, n-hexyl n-octyl ether, n-octyl n-decyl ether, n-decyl n-undecyl ether, n-undecyl n-dodecyl ether and n-hexyl n-undecyl ether as well as di-tert-butyl ether, di-iso-pentyl ether, di-3-ethyldecyl ether, tert.-butyl n-octyl ether, iso-pentyl n-octyl ether and 2-methylpentyl n-octyl ether,
- fatty alcohols, particularly linear and/or saturated fatty alcohols with 8 to 30 carbon atoms,
- monoesters of C_8 to C_{30} fatty acids with alcohols with 6 to 24 carbon atoms,
- fiber-structure-improving agents, particularly mono-, di- and oligosaccharides such as, for example, glucose, galactose, fructose and lactose,
- conditioners, such as paraffin oils, vegetal oils e.g. sunflower oil, orange oil, almond oil, wheat germ oil and peach kernel oil as well as
- quaternized amines, such as methyl-1-alkylamidoethyl-2-alkylimidazolinium methosulfate,
- defoamers, such as silicones,
- dyestuffs for coloring the preparation,
- anti-dandruff agents, such as piroctone oleamine, zinc omadine and climbazol,
- active substances, such as allantoin and bisabolol,

- cholesterol,
- consistency factors, such as sugar esters, polyol esters or polyol alkyl ethers,
- fats and waxes, such as spermaceti, beeswax, montan wax and paraffins,
- fatty acid alkanolamides,
- complexing agents, such as EDTA, NTA, β-alanine diacetic acid and phosphonic acids,
- swelling and penetration agents, such as primary, secondary and tertiary phosphates,
- opacifiers, such as latex, styrene/PVP- and styrene/acrylamide copolymers,
- pearlizers, such as ethylene glycol mono- and distearate and PEG-3-distearate,
- pigments,
- reducing agents, such as, for example, thioglycolic acid and its derivatives, thiolactic acid, cysteamine, thiomalic acid and α-mercaptoethanesulfonic acid,
- propellants, such as propane/butane mixtures, N_2O, dimethyl ether, CO_2 and air,
- antioxidants.

Information on other optional components and the quantities in which they are used can be found in the reference books known to the expert, for example the monograph by K.H. Schrader cited above.

In a further embodiment of the teaching according to the invention, it can be preferred to mix the active substance complex (A) directly into dyestuffs or toners, that means utilizing the inventive active substance complex (A) in combination with dyestuffs and/or dyestuff precursors.

Oxidation dyestuff precursors of the developer type (B1) that are used are normally primary aromatic amines with an additional free or substituted hydroxyl or amine group in the para or ortho position, diaminopyridine derivatives,

heterocyclic hydrazones, 4-aminopyrazole derivatives as well as 2,4,5,6-tetraamino pyrimidine and derivatives thereof. Suitable developer components are, for example, p-phenylenediamine, p-toluylenediamine, p-aminophenol, o-aminophenol, 1-(2'hydroxyethyl)-2,5-diaminobenzene, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, 2-(2,5-diamino-phenoxy)ethanol,4-amino-3-methylphenol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2-dimethylamino-4,5,6-triaminopyrimidine,2-hydroxymethylamino-4-aminophenol, bis-(4-aminophenyl)amine, 4-amino-3-fluorophenol, 2-aminomethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 4-amino-2-((diethylamino)-methyl)phenol, bis-(2-hydroxy-5-aminophenyl)methane, 1,4-bis-(4-aminophenyl)diazacycloheptane, 1,3-bis-(N(2-hydroxyethyl)-N(4-aminophenylamino))-2-propanol, 4-amino-2-(2-hydroxyethoxy)phenol, 1,10-bis-(2,5-diaminophenyl)-1,4,7,10-tetraoxadecane as well as 4,5-diaminopyrazol derivatives according to EP 0 740 931 or WO 94/08970 such as for example 4,5-diamino-1-(2'-hydroxyethyl)pyrazole. Particularly advantageous developer components are p-phenylenediamine, p-toluylenediamine, p-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, 4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine.

Oxidation dyestuff precursors of the coupler type (B2) that are usually used are m-phenylenediamine derivatives, naphthols, resorcinol und resorcinol derivatives, pyrazolones und m-aminophenol derivatives. Exemplary coupler components are

- m-aminophenol und its derivatives such as for example 5-amino-2-methylphenol, 5-(3-hydroxypropylamino)-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 2-hydroxy-4-aminophenoxyethanol, 2,6-dimethyl-3-aminophenol, 3-trifluoroacetylamino-2-chloro-6-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5- (2'-hydroxyethyl)-amino-2-methylphenol, 3-(diethylamino)-phenol, N-cyclopentyl-3-aminophenol, 1,3-dihydroxy-5-

(methylamino)-benzene, 3-(ethylamino)-4-methylphenol and 2,4-dichloro-3-aminophenol,

- o-aminophenol and its derivatives,
- m-diaminobenzene and its derivatives such as, for example 2,4-diaminophenoxyethanol, 1,3-bis-(2, 4-diaminophenoxy)propane, 1-methoxy-2-amino-4-(2'-hydroxy- ethylamino) benzeneol, 1,3-bis-(2,4-diaminophenyl)propane, 2,6-bis-(2-hydroxyethyl-amino)-1-methylbenzene and 1-amino-3-bis-(2'-hydroxyethyl)aminobenzene,
- o-diaminobenzene and its derivatives such as, for example 3,4-diaminobenzoic acid and 2,3-diamino-1-methylbenzene,
- di-or trihydroxybenzene derivatives such as, for example resorcinol, resorcinol-monomethyl ether, 2-methylresorcinol, 5-methylresorcinol, 2,5-dimethylresorcinol, 2-chlororesorcinol, 4-chlororesorcinol, pyrogallol and 1,2,4-trihydroxybenzene,
- pyridine derivatives such as, for example 2,6-dihydroxypyridine, 2-amino-3- hydroxypyridine, 2-amino-5-chloro-3-hydroxypyridine, 3-amino-2-methylamino-6- methoxypyridine, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dihydroxy-4-methylpyridine, 2,6-diaminopyridine, 2,3-diamino-6-methoxypyridine and 3,5-diamino-2,6-dimethoxypyridine,
- naphthalene derivatives such as, for example 1-naphthol, 2-methyl-1-naphthol, 2-hydroxymethyl-1-naphthol, 2-hydroxyethyl-1-naphthol, 1,5-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 1,8-dihydroxynaphthalene, 2,7-dihydroxynaphthalene and 2,3-dihydroxynaphthalene,
- morpholine derivatives such as, for example 6-hydroxybenzomorpholine und 6-amino- benzomorpholine, quinoxaline derivatives such as 6-methyl-1,2,3,4- tetrahydroquinoxaline,
- pyrazole derivatives such as, for example 1-phenyl-3-methylpyrazol-5-one, indole derivatives such as, for example 4-hydroxyindole, 6-hydroxyindole und 7-hydroxyindole, methylenedioxybenzene derivatives such as, for example 1-hydroxy-3,4-

methylenedioxybenzene, 1-amino-3,4-methylenedioxybenzene and 1-(2'-hydroxyethyl)-amino-3,4-methylenedioxybenzene.

Particularly suitable coupler components are 1-naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, 3-aminophenol, 5-amino-2-methylphenol, 2-amino-3-hydroxypyridine, resorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methylresorcinol, 5-methylresorcinol, 2,5-dimethylresorcinol and 2,6-dihydroxy-3,4-dimethylpyridine.

Substantive dyestuffs are normally nitrophenylenediamines, nitroaminophenols, azodyes, anthrachinones or indophenols. Particularly suitable substantive dyestuffs are known compounds under the international names or trade names HC Yellow 2, HC Yellow 4, HC Yellow 5, HC Yellow 6, Basic Yellow 57, Disperse Orange 3, HC Red 3, HC Red BN, Basic Red 76, HC Blue 2, HC Blue 12, Disperse Blue 3, Basic Blue 99, HC Violet 1, Disperse Violet 1, Disperse Violet 4, Disperse Black 9, Basic Brown 16 und Basic Brown 17 as well as 1,4-bis-(β-hydroxyethyl)-amino-2-nitrobenzene, 4-amino-2-nitrodiphenylamine-2'-carboxylic acid, 6-nitro-1,2,3,4-tetrahydroquinoxaline, hydroxyethyl-2-nitrotoluidine, picramic acid, 2-amino-6-chloro-4-nitrophenol, 4-ethylamino-3-nitrobenzoic acid and 2-chloro-6-ethylamino-1-hydroxy-4-nitrobenzene.

Naturally occurring substantive dyes comprise, for example, henna red, henna neutral, camomile blossom, sandalwood, black tea, buckthorn bark, sage, logwood, madder root, catechu, cedar and alkanet root.

Indoles and indolines as well as their physiologically compatible salts are used as precursors of natural dye analogs. Preferably, such indoles and indolines are used that have at least one hydroxy or amine group, preferably as a substituent on the six-membered ring. These groups may be further substituted e.g. in the form of etherified or esterified hydroxyl groups or by alkylated amino groups. Particularly advantageous properties are shown by 5,6-dihydroxyindoline, N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-

dihydroxyindoline, N-butyl-5,6-dihydroxyindoline, 5,6-dihydroxyindoline-2-carboxylic acid, 6-hydroxyindoline, 6-aminoindoline and 4-aminoindoline, and 5,6-dihydroxyindole, N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole, 5,6-dihydroxyindole-2-carboxylic acid, 6-hydroxyindole, 6-aminoindole and 4-aminoindole.

Within this group, particular emphasis is given to N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline and, in particular, 5,6-dihydroxyindoline and N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole and, especially 5,6-dihydroxyindole.

The indoline and indole derivatives in the dyestuffs used in the context of the inventive process can be added either as free bases or else in the form of their physiologically compatible salts of inorganic or organic acids, e.g. the hydrochlorides, the sulfates and hydrobromides.

When using dyestuff precursors of the indoline or indole type, it may be preferred to use these together with at least one amino acid and/or at least one oligopeptide. Preferred amino acids are aminocarboxylic acids, in particular α-aminocarboxylic acids and ω-aminocarboxylic acids. Of the α-aminocarboxylic acids, arginine, lysine, ornithine and histidine are again particularly preferred. A quite particularly preferred amino acid is arginine, in particular in free form, but also used as the hydrochloride.

The inventive compositions comprise both the oxidative dyestuff precursors and also the substantive dyes and the precursors of the natural dye analogs in amounts from 0.01 to 20 wt.%, preferably 0.1 to 5 wt.%, each based on the total composition.

Hair colorants, particularly if the coloration is carried out oxidatively, whether with atmospheric oxygen or other oxidizing agents such as hydrogen peroxide, are usually adjusted to be slightly acidic to alkaline, i.e. to pH values in the range from about 5 to 11. For this purpose, the colorants comprise alkalinizing agents, usually alkali metal or alkali earth hydroxides, ammonia or organic amines. Preferred alkalinizing agents are monoethanolamine, monoisopropanolamine, 2-amino-2-methylpropanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-methylbutanol and triethanolamine, and also alkali metal and alkaline earth metal hydroxides. In particular, monoethanolamine, triethanolamine and 2-amino-2-methylpropanol and 2-amino-2-methyl-1,3-propanediol are preferred within this group. The use of ω-amino acids, such as ω-aminocaproic acid, as alkalinizing agents is also possible.

If the actual hair colors are formed in the course of an oxidative process, then customary oxidizing agents, such as, in particular, hydrogen peroxide or its addition products to urea, melamine or sodium borate, can be used. The oxidation with atmospheric oxygen as the sole oxidizing agent may, however, be preferred. In addition, it is possible to carry out the oxidation using enzymes, where the enzymes are used both for generating oxidizing percompounds, and also for enhancing the action of a small amount of oxidizing agent present, or else enzymes are used which transfer electrons from suitable developer components (reducing agents) to atmospheric oxygen. Preference is given here to oxidases, such as tyrosinase, ascorbate oxidase and laccase. Mention may also be made of the procedure to enhance the action of small amounts (e.g. 1% and below, based on the overall composition) of hydrogen peroxide using peroxidases.

Expediently, the preparation of the oxidizing agent is then mixed with the preparation containing the dye precursors immediately prior to dyeing the hair. The ready-to-use hair-coloring preparation thus formed should preferably have a pH in the range from 6 to 10. Use of the hair colorant in a weakly alkaline

medium is particularly preferred. The application temperatures can be in a range between 15 and 40°C, preferably at the temperature of the scalp. After a contact time of about 5 to 45, in particular 15 to 30 minutes, the hair colorant is removed by rinsing it out of the hair being dyed. A rewash with a shampoo is dispensed with if a strongly surfactant-containing carrier, e.g. a color shampoo, has been used.

Surprisingly, it was found that keratinous fibers, which were colored with preparations comprising sericin and fibroin and/or their derivatives in combination with special polymers, exhibit significantly increased properties.

Accordingly, a second subject of the present invention are compositions for coloring keratinous fibers comprising, in a cosmetically acceptable carrier,

- at least one dyestuff precursor (FV)
- an active substance complex (A), consisting of
  - o an active substance (A1), selected from sericin and/or sericin hydrolyzates and/or their derivatives and/or their mixtures, and
  - o an active substance (A2), selected from fibroin and/or its hydrolyzates and/or its derivatives and/or mixtures thereof, as well as
- an amphoteric polymer (AP).

According to the invention, keratinous fibers are understood to mean furs, wool, feathers and particularly human hair.

The inventive combination of active substance complex (A) and amphoteric polymer (AP) significantly improves the previously cited important internal and external structural characteristics and the strength as well as the elasticity of human hair.

Regarding the detailed specifications of the active substance complex (A), suffice it here to refer to the statements made further above.

The inventive hair colorants comprise the active substance complex (A) in amounts from 0.001 – 10 wt.%, based on the total composition. Amounts from 0.001 to 5 wt.%, particularly 0.005 to 1 wt.% are quite particularly preferred.

The inventive compositions being used comprise, in addition to the active substance complex (A) at least one amphoteric polymer (AP). The term amphoteric polymers according to the invention, covers both, those polymers which have both free amino groups as well as free -COOH or SO_3H groups in the molecule and are capable of forming internal salts, as well as zwitterionic polymers that contain quaternary ammonium groups and $-COO^-$ or $-SO_3^-$ groups in the molecule, and those polymers which contain -COOH or SO_3H groups and quaternary ammonium groups.

Examples of amphopolymers which can be used according to the invention are those commercial products with the name Amphomer® from National Starch Company. Typical representatives are the copolymers of tert-butylaminoethyl methacrylate, N-(1,1,3,3-tetramethylbutyl)acrylamide as well as two or more monomers from the group acrylic acid, methacrylic acid and simple esters thereof, said copolymers having the INCI name octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer. In this group are found, for example, the commercial products Amphomer® 028-4910 and Amphomer® LV 71. Additionally, the commercial product Amphomer® HC (INCI name: acrylates/octylacrylamide copolymer) may be cited.

Further amphoteric polymers which can be used according to the invention are the compounds cited in British laid-open specification 2 104 091, European laid-open specification 47 714, European laid-open specification 217 274, European laid-open specification 283 817 and German laid-open specification 28 17 369.

Preferred amphoteric polymers used are those polymers that are composed essentially of

(a) monomers with quaternary ammonium groups of the general formula (I),

R^1-CH=CR^2-CO-Z-(C_nH_{2n})-$N^{(+)}R^3R^4R^5$ $A^{(-)}$ (I)

in which R^1 and R^2, independently of one another, are hydrogen or a methyl group, and R^3, R^4 and R^5, independently of one another, are alkyl groups having 1 to 4 carbon atoms, Z is an NH group or an oxygen atom, n is a whole number from 2 to 5 and $A^{(-)}$ is the anion of an organic or inorganic acid and

(b) monomeric carboxylic acids of the general formula (II),

R^6-CH=CR^7-COOH (II)

in which R^6 and R^7, independently of one another, are hydrogen or methyl groups.

These compounds can be used in accordance with the invention both directly as well as in salt form, which is obtained by neutralization of the polymers, for example with an alkali hydroxide. With regard to the details of the preparation of these polymers, reference is made expressly to the content of German laid-open specification 39 29 973. Quite particular preference is given to those polymers in which monomers of type (a) are used in which R^3, R^4 and R^5 are methyl groups. In addition, monomers of type (a) may be preferred in which Z is an NH group. In addition, the anion $A^{(-)}$ in the monomers of type (a) is preferably a halide, methoxysulfate or ethoxysulfate ion; acrylamidopropyltrimethylammonium chloride is a particularly preferred monomer (a). The monomer (b) used for said polymers is preferably acrylic acid.

Preferably, the amphoteric polymers are used in the inventive compositions in amounts from 0.001 to 5 wt.%. Amounts of 0.1 to 3 wt.% are particularly preferred. The given amounts are each based on the dye preparation, i.e. where required on the mixture of the actual colorant cream and the care components, without the added oxidizing agent preparation where used.

The present invention is not at all subject to any limitations concerning further applicable dyestuff precursors (FV) in the inventive colorants. The inventive colorants may comprise as dyestuff precursors

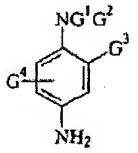
- oxidation dyestuff precursors of the developer and/or coupler type, and
- precursors of dyes that are analogous to natural dyes, such as indole derivatives and indoline derivatives

as well as mixtures of representatives of these groups.

In the context of a first preferred embodiment of the present invention, the inventive compositions comprise at least one dyestuff precursor of the developer and/or coupler type.

Developer components used are usually aromatic primary amines, with a further free or substituted hydroxyl or amino group in the para or ortho position, diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazole derivatives as well as 2,4,5,6-tetraaminopyrimidine and its derivatives.

According to the invention, it can be preferred to use a p-phenylenediamine derivative or one of its physiologically compatible salts as the developer component. p-Phenylenediamine derivatives of formula (E1) are particularly preferred



(E1)

in which

- G^1 stands for a hydrogen atom, a C_1 to C_4 alkyl radical, a C_1 to C_4 monohydroxyalkyl radical, a C_2 to C_4 polyhydroxyalkyl radical, a (C_1 to C_4) -alkoxy-(C_1 to C_4)-alkyl radical, a 4'-aminophenyl radical or a C_1 to C_4 alkyl radical substituted by a nitrogen-containing group, a phenyl radical or a 4'-aminophenyl radical;
- G^2 stands for a hydrogen atom, a C_1 to C_4 alkyl radical, a C_1 to C_4 monohydroxyalkyl radical, a C_2 to C_4 polyhydroxyalkyl radical, a (C_1 to C_4)-

alkoxy-(C_1 to C_4)-alkyl radical or a C_1 to C_4 alkyl radical substituted by a nitrogen-containing group;

- G^3 stands for a hydrogen atom, a halogen atom, such as a chlorine, bromine, iodine or fluorine atom, a C_1 to C_4 alkyl radical, a C_1 to C_4 monohydroxyalkyl radical, a C_2 to C_4 polyhydroxyalkyl radical, a C_1 to C_4 hydroxyalkoxy radical, a C_1 to C_4 acetylaminoalkoxy radical, a C_1 to C_4 mesylaminoalkoxy radical or a C_1 to C_4 carbamoylaminoalkoxy radical;
- G^4 is a hydrogen atom, a halogen atom or a C_1 to C_4 alkyl radical or
- if G^3 and G^4 are in the ortho position to one another, they may together form a bridging α,ω-alkylenedioxo group such as, for example, an ethylenedioxy group.

Examples of substituents of the cited C_1 to C_4 alkyl radicals in the inventive compounds are the methyl, ethyl, propyl, isopropyl and butyl groups. Ethyl and methyl are preferred alkyl radicals. According to the invention, preferred C_1 to C_4 alkoxy radicals are, for example, methoxy or ethoxy groups. In addition, preferred examples of a C_1 to C_4 hydroxyalkyl group can be cited as a hydroxymethyl, a 2-hydroxyethyl, a 3-hydroxypropyl or a 4-hydroxybutyl group. A 2-hydroxyethyl group is particularly preferred. A particularly preferred C_2 to C_4 polyhydroxyalkyl group is the 1,2-dihydroxyethyl group. According to the invention, examples of halogen atoms are F, Cl or Br atoms, Cl atoms are quite particularly preferred. According to the invention, the terms used later are derived from the definitions given here. Examples of nitrogen-containing groups of formula (E1) are particularly the amino groups, C_1 to C_4 monoalkylamino groups, C_1 to C_4 dialkylamino groups, C_1 to C_4 trialkylamino groups, C_1 to C_4 monohydroxyalkylamino groups, imadazolinium and ammonium.

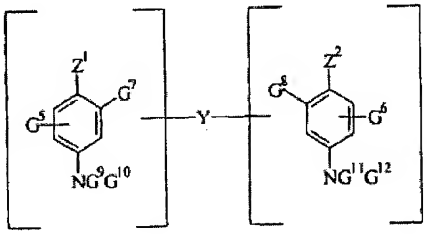
Particularly preferred p-phenylenediamines corresponding to formula (E1) are selected from p-phenylenediamine, p-toluylenediamine, 2-chloro-p-phenylenediamine, 2,3-dimethyl-p-phenylenediamine, 2,6-dimethyl-p-phenylenediamine, 2,6-diethyl-p-phenylenediamine, 2,5-dimethyl-p-phenylenediamine, N,N-dimethyl-p-phenylenediamine, N,N-diethyl-p-

phenylenediamine, N,N-dipropyl-p-phenylenediamine, 4-amino-3-methyl-(N,N-diethyl)-aniline, N,N-bis-(β-hydroxyethyl)-p-phenylenediamine, 4-N,N-bis-(β-hydroxyethyl)-amino-2-methylaniline, 4-N,N-bis-(β-hydroxyethyl)-amino-2-chloroaniline, 2-(β-hydroxyethyl)-p-phenylenediamine, 2-fluoro-p-phenylenediamine, 2-isopropyl-p-phenylenediamine, N-(β-hydroxypropyl)-p-phenylenediamine, 2-hydroxymethyl-p-phenylenediamine, N,N-dimethyl-3-methyl-p-phenylenediamine, N,N-(ethyl-β-hydroxyethyl)-p-phenylene-diamine, N-(β,γ-dihydroxypropyl)-p-phenylenediamine, N-(4'-aminophenyl)-p-phenylenediamine, N-phenyl-p-phenylenediamine, 2-(β-hydroxyethyloxy)-p-phenylenediamine, 2-(β-acetylaminoethyloxy)-p-phenylenediamine, N-(β-methoxyethyl)-p-phenylenediamine and 5,8-diaminobenzo-1,4-dioxane and their physiologically compatible salts.

According to the invention, quite particularly preferred p-phenylenediamine derivatives corresponding to formula (E1) are p-phenylenediamine, p-toluylenediamine, 2-(β-hydroxyethyl)-p-phenylenediamine and N,N-bis(β-hydroxyethyl)-p-phenylenediamine.

According to the invention, it can be further preferred to use developer components that are compounds comprising at least two aromatic nuclei substituted by amino and/or hydroxyl groups.

The binuclear developer components, which may be used in the coloring compositions according to the invention, include in particular compounds corresponding to formula (E2) as well as their physiologically compatible salts:



(E2)

in which:

- Z^1 and Z^2 independently of one another stand for a hydroxyl or NH_2 radical which is optionally substituted by a C_1 to C_4 alkyl radical, by a C_1 to C_4 hydroxyalkyl radical and/or by a bridging group Y or which is optionally part of a bridging ring system,
- the bridging group Y is an alkylene group with 1 to 14 carbon atoms, such as, for example, a linear or branched alkylene chain or an alkylene ring which may be interrupted or terminated by one or more nitrogen-containing groups and/or one or more hetero atoms, such as oxygen, sulfur or nitrogen atoms, and may optionally be substituted by one or more hydroxyl or C_1 to C_8 alkoxy radicals or is a direct bond,
- G^5 and G^6 independently of one another stand for a hydrogen or halogen atom, a C_1 to C_4 alkyl radical, a C_1 to C_4 monohydroxyalkyl radical, a C_2 to C_4 polyhydroxyalkyl radical, a C_1 to C_4 aminoalkyl radical or a direct bond to the bridging group Y,
- G^7, G^8, G^9, G^{10}, G^{11} and G^{12} independently of one another stand for a hydrogen atom, a direct bond to the bridging group Y or a C_1 to C_4 alkyl radical,

with the provisos that

- the compounds of formula (E2) contain only one bridging group Y per molecule and
- the compounds of formula (E2) contain at least one amino group that carries at least one hydrogen atom.

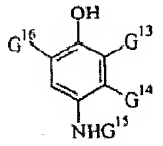
According to the invention, the substituents used in formula (E2) are as defined in the foregoing embodiments.

Preferred binuclear primary intermediates corresponding to formula (E2) are, in particular, N,N'-bis-(β-hydroxyethyl)-N,N'-bis-(4'-aminophenyl)-1,3-diaminopropan-2-ol, N,N'-bis-(β-hydroxyethyl)-N,N'-bis-(4'-amino-phenyl)-ethylenediamine, N,N'-bis-(4-aminophenyl)-tetramethylene diamine, N,N'-bis-(β-hydroxyethyl)-N,N'-bis-(4'-aminophenyl)-tetra-methylenediamine, N,N'-bis-(4-methylaminophenyl)-tetramethylene diamine, N,N'-bis-(ethyl)-N,N'-bis-(4'-

amino-3'-methylphenyl)-ethylene-diamine, bis-(2-hydroxy-5-aminophenyl)-methane, 1,4-bis-(4'-amino-phenyl)-diazacycloheptane, N,N'-bis-(2-hydroxy-5-aminobenzyl)-piperazine, N-(4'-aminophenyl)-p-phenylenediamine and 1,10-bis-(2',5'-diaminophenyl)-1,4,7,10-tetraoxadecane and their physiologically compatible salts.

Quite particularly preferred binuclear primary intermediates corresponding to formula (E2) are N,N'-bis-(β-hydroxyethyl)-N,N'-bis-(4'-aminophenyl)-1,3-diaminopropan-2-ol, bis-(2-hydroxy-5-aminophenyl)-methane, N,N'-bis-(4'-aminophenyl)-1,4-diazacycloheptane and 1,10-bis-(2',5'-diaminophenyl)-1,4,7,10-tetraoxadecane or one of their physiologically compatible salts.

According to the invention, it can be preferred to use a p-aminophenol derivative or one of its physiologically compatible salts as the developer component. p-Aminophenol derivatives of formula (E3) are particularly preferred



(E3)

in which:

- G^{13} stands for a hydrogen atom, a halogen atom, a C_1 to C_4 alkyl radical, a C_1 to C_4 monohydroxyalkyl radical, a C_2 to C_4 polyhydroxyalkyl radical, a (C_1 to C_4)-alkoxy-(C_1 to C_4)-alkyl radical, a C_1 to C_4 aminoalkyl radical, a hydroxy-(C_1 to C_4)-alkylamino radical, a C_1 to C_4 hydroxyalkyoxy radical, a C_1 to C_4 hydroxyalkyl-(C_1 to C_4)-aminoalkyl radical or a (di-C_1 to C_4 alkylamino)-(C_1 to C_4)-alkyl radical,
- G^{14} stands for a hydrogen atom or a halogen atom, a C_1 to C_4 alkyl radical, a C_1 to C_4 hydroxyalkyl radical, a C_2 to C_4 polyhydroxyalkyl radical, a (C_1 to C_4)-alkoxy-(C_1 to C_4)-alkyl radical, a C_1 to C_4 aminoalkyl radical or a C_1 to C_4 cyanoalkyl radical,

- G^{15} stands for hydrogen, a C_1 to C_4 alkyl radical, a C_1 to C_4 hydroxyalkyl radical, a C_2 to C_4 polyhydroxyalkyl radical, a phenyl radical or a benzyl radical and
- G^{16} stands for hydrogen or a halogen atom.

According to the invention, the substituents used in formula (E3) are defined as in the foregoing embodiments.

Preferred p-aminophenols corresponding to formula (E3) are, in particular, p-aminophenol, N-methyl-p-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 2-hydroxymethylamino-4-aminophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-(2-hydroxyethoxy)-phenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(β-hydroxyethylaminomethyl)-phenol, 4-amino-2-(α,β-dihydroxyethyl)-phenol, 4-amino-2-fluorophenol, 4-amino-2-chlorophenol, 2,6-dichloro-4-aminophenol, 4-amino-2-(diethylaminomethyl)-phenol and their physiologically compatible salts.

Quite particularly preferred compounds corresponding to formula (E3) are p-aminophenol, 4-amino-3-methylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(α,β-dihydroxyethyl)-phenol and 4-amino-2-(diethylaminomethyl)-phenol.

The developer component may also be selected from o-aminophenol and derivatives thereof such as, for example, 2-amino-4-methylphenol, 2-amino-5-methylphenol or 2-amino-4-chlorophenol.

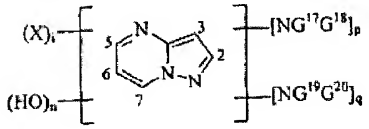
The developer component may also be selected from heterocyclic developer components such as, for example, the pyridine, pyrimidine, pyrazole, pyrazole/pyrimidine derivatives and physiologically compatible salts thereof.

Preferred pyridine derivatives are particularly the compounds described in the patents GB 1 026 978 and GB 1 153 196, such as 2,5-diaminopyridine, 2-(4'-methoxyphenyl)-amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-(β-methoxyethyl)-amino-3-amino-6-methoxypyridine and 3,4-diaminopyridine.

Preferred pyrimidine derivatives are, in particular, the compounds described in German patent DE 2 359 399, Japanese laid-open patent JP 02019576 A2 or the laid-open patent WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2-dimethylamino-4,5,6-triamino-pyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-triaminopyrimidine.

Preferred pyrazole derivatives are, in particular, the compounds described in the patents DE 3 843 892, DE 4 133 957 and patent applications WO 94/08969, WO 94/08970, EP 740 931 and DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-(β-hydroxyethyl)-pyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)-pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methyl pyrazole, 4,5-diamino-3-tert.butyl-1-methylpyrazole, 4,5-diamino-1-tert.butyl-3-methylpyrazole, 4,5-diamino-1-(β-hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)-pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2'-aminoethyl)-amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-methylaminopyrazole and 3,5-diamino-4-(β-hydroxyethyl)-amino-1-methylpyrazole.

Preferred pyrazole-pyrimidine derivatives are, in particular, the derivatives of pyrazole-[1,5-a]-pyrimidine corresponding to formula (E4) below and tautomeric forms thereof, in so far that a tautomeric equilibrium exists:



(E4)

in which:

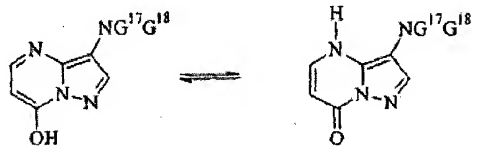
- G^{17}, G^{18}, G^{19} and G^{20} independently of one another stand for a hydrogen atom, a C_1 to C_4 alkyl radical, an aryl radical, a C_1 to C_4 hydroxyalkyl radical, a C_2 to C_4 polyhydroxyalkyl radical, a (C_1 to C_4)-alkoxy-(C_1 to C_4)-alkyl radical, a C_1 to C_4 aminoalkyl radical which may optionally be protected by an acetylureido or sulfonyl radical, a (C_1 to C_4)-alkylamino-(C_1 to C_4)-alkyl radical, a di[(C_1 to C_4)-alkyl]-(C_1 to C_4)-aminoalkyl radical, the dialkyl radicals optionally forming a carbon cycle or a heterocycle with 5 or 6 members, a C_1 to C_4 hydroxyalkyl or a di-(C_1 to C_4)-[hydroxyalkyl]-(C_1 to C_4)-aminoalkyl radical;
- the X radicals independently of one another stand for a hydrogen atom, a C_1 to C_4 alkyl radical, an aryl radical, a C_1 to C_4 hydroxyalkyl radical, a C_2 to C_4 polyhydroxyalkyl radical, a C_1 to C_4 aminoalkyl radical, a (C_1 to C_4)-alkylamino-(C_1 to C_4)-alkyl radical, a di[(C_1 to C_4)-alkyl]-(C_1 to C_4)-aminoalkyl radical, the dialkyl radicals optionally forming a carbon cycle or a heterocycle with 5 or 6 members, a C_1 to C_4 hydroxyalkyl or a di-(C_1 to C_4)-[hydroxyalkyl]-(C_1 to C_4)-aminoalkyl radical, an amino radical, a C_1 to C_4 alkyl or a di-(C_1 to C_4 -hydroxyalkyl)-amino radical, a halogen atom, a carboxylic acid group or a sulfonic acid group,
- i has the value 0, 1, 2 or 3,
- p has the value 0 or 1,
- q has the value 0 or 1 and
- n has the value 0 or 1,

with the proviso that

- the sum of p+q is not 0,
- where p+q = 2, n has the value 0 and the groups $NG^{17}G^{18}$ and $NG^{19}G^{20}$ occupy the (2,3); (5,6); (6,7); (3,5) or (3,7) positions;
- where p+q = 1, n has the value 1 and the groups $NG^{17}G^{18}$ (or $NG^{19}G^{20}$) and the group OH occupy the (2,3); (5,6); (6,7); (3,5) or (3,7) positions;

According to the invention, the substituents used in formula (E4) are as defined in the foregoing embodiments.

If the pyrazole-[1,5-a]-pyrimidine corresponding to formula (E4) above contains a hydroxy group in one of the positions 2, 5 or 7 of the ring system, a tautomeric equilibrium exists as illustrated, for example, in the following scheme:



Among the pyrazole-[1,5-a]-pyrimidines corresponding to formula (E4) above, the following may be particularly mentioned:

- pyrazole-[1,5-a]-pyrimidine-3,7-diamine;
- 2,5-dimethylpyrazole-[1,5-a]-pyrimidine-3,7-diamine;
- pyrazole-[1,5-a]-pyrimidine-3,5-diamine;
- 2,7-dimethylpyrazole-[1,5-a]-pyrimidine-3,5-diamine;
- 3-aminopyrazole-[1,5-a]-pyrimidin-7-ol;
- 3-aminopyrazole-[1,5-a]-pyrimidin-5-ol;
- 2-(3-aminopyrazole-[1,5-a]-pyrimidin-7-ylamino)-ethanol;
- 2-(7-aminopyrazole-[1,5-a]-pyrimidin-3-ylamino)-ethanol;
- 2-[(3-aminopyrazole-[1,5-a]-pyrimidin-7-yl)-(2-hydroxyethyl)-amino]-ethanol;
- 2-[(7-aminopyrazole-[1,5-a]-pyrimidin-3-yl)-(2-hydroxyethyl)-amino]-ethanol;
- 5,6-dimethylpyrazole-[1,5-a]-pyrimidine-3,7-diamine;
- 2,6-dimethylpyrazole-[1,5-a]-pyrimidine-3,7-diamine;
- 3-amino-7-dimethylamino-2,5-dimethylpyrazole-[1,5-a]-pyrimidine;

and their physiologically compatible salts and their tautomeric forms if a tautomeric equilibrium exists.

The pyrazole-[1,5-a]-pyrimidines corresponding to formula (V) above may be prepared by cyclization starting from an aminopyrazole or from hydrazine, as described in the literature.

In a further preferred embodiment, the inventive colorants comprise at least one coupler component.

The coupler components used are, in general, m-phenylenediamine derivatives, naphthols, resorcinol and resorcinol derivatives, pyrazolones and m-aminophenol derivatives. Particularly suitable coupler substances are: 1-naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthaline, 5-amino-2-methylphenol, m-aminophenol, resorcinol, resorcinol monomethyl ether, m-phenylenediamine, 1-phenyl-3-methyl-pyrazolone-5, 2,4-dichloro-3-aminophenol, 1,3-bis-(2',4'-diaminophenoxy)propane, 2-chlororesorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-amino-3-hydroxypyridine, 2-methylresorcinol, 5-methylresorcinol and 2-methyl-4-chloro-5-aminophenol.

According to the invention, preferred coupler components are

- m-aminophenol and derivatives thereof such as, for example, 5-amino-2-methylphenol, N-cyclopentyl-3-aminopenol, 3-amino-2-chloro-6-methylphenol, 2-hydroxy-4-aminophenoxyethanol, 2,6-dimethyl-3-aminophenol, 3-trifluoroacetylamino-2-chloro-6-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-(2'-hydroxyethyl)-amino-2-methylphenol, 3-(diethylamino)-phenol, N-cyclopentyl-3-aminophenol, 1,3-dihydroxy-5-(methylamino)-benzene, 3-(ethylamino)-4-methylphenol and 2,4-dichloro-3-aminophenol,
- o-aminophenol and derivatives thereof,
- m-diaminobenzene and derivatives thereof such as, for example, 2,4-diaminophenoxyethanol, 1,3-bis-(2',4'-diaminophenoxy)-propane, 1-methoxy-2-amino-4-(2'-hydroxyethylamino)-benzene, 1,3-bis-(2',4'-

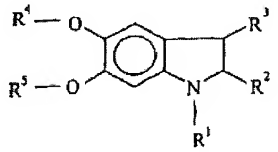
diaminophenyl)-propane, 2,6-bis-(2'-hydroxyethylamino)-1-methylbenzene and 1-amino-3-bis-(2'-hydroxyethyl)-aminobenzene,

- o-diaminobenzene and derivatives thereof such as, for example, 3,4-diaminobenzoic acid and 2,3-diamino-1-methylbenzene,
- di- and trihydroxybenzene derivatives such as, for example, resorcinol, resorcinol monomethyl ether, 2-methyl resorcinol, 5-methyl resorcinol, 2,5-dimethyl resorcinol, 2-chlororesorcinol, 4-chlororesorcinol, pyrogallol and 1,2,4-trihydroxybenzene,
- pyridine derivatives such as, for example, 2,6-dihydroxypyridine, 2-amino-3-hydroxypyridine, 2-amino-5-chloro-3-hydroxypyridine, 3-amino-2-methylamino-6-methoxypyridine, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dihydroxy-4-methylpyridine, 2,6-diamino-pyridine, 2,3-diamino-6-methoxypyridine and 3,5-diamino-2,6-dimethoxypyridine,
- naphthalene derivatives such as, for example, 1-naphthol, 2-methyl-1-naphthol, 2-hydroxymethyl-1-naphthol, 2-hydroxyethyl-1-naphthol, 1,5-dihydroxynaphthalene, 1,6-dihdroxynaphthalene, 1,7-dihdroxy-naphthalene, 1,8-dihdroxynaphthalene, 2,7-dihdroxynaphthalene and 2,3-dihdroxynaphthalene,
- morpholine derivatives such as, for example, 6-hydroxybenzomorpholine and 6-aminobenzomorpholine,
- quinoxaline derivatives such as, for example, 6-methyl-1,2,3,4-tetrahydroquinoxaline,
- pyrazole derivatives such as, for example, 1-phenyl-3-methylpyrazol-5-one,
- indole derivatives such as, for example, 4-hydroxyindole, 6-hydroxyindole and 7-hydroxyindole,
- pyrimidine derivatives such as, for example, 4,6-diaminopyrimidine, 4-amino-2,6-dihydroxypyrimidine, 2,4-diamino-6-hydroxypyrimidine, 2,4,6-trihydroxypyrimidine, 2-amino-4-methylpyrimidine, 2-amino-4-hydroxy-6-methylpyrimidine and 4,6-dihydroxy-2-methylpyrimidine or
- methylenedioxybenzene derivatives such as, for example, 1-hydroxy-3,4-methylenedioxybenzene, 1-amino-3,4-methylene-dioxybenzene and 1-(2'-hydroxyethyl)-amino-3,4-methylene-dioxybenzene.

According to the invention, particularly preferred coupling components are1-naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthaline, 3-aminophenol, 5-amino-2-methylphenol, 2-amino-3-hydroxypyridine, resorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methylresorcinol, 5-methylresorcinol, 2,5-dimethylresorcinol and 2,6-dihydroxy-3,4-dimethylpyridine.

In a further embodiment of the present invention, the colorants comprise at least one precursor of a natural dye analog as the dyestuff precursor (FV). Preferred precursors of natural dye analogs are indoles and/or indolines containing at least one hydroxy or amino group, preferably as a substituent on the six-membered ring. These groups may carry further substituents, for example in the form of an etherification or esterification of the hydroxyl group or an alkylation of the amino group. In a second preferred embodiment, the colorants comprise at least one indole and/or indoline derivative.

Particularly suitable precursors of natural hair-dye analogs are derivatives of 5,6-dihydroxyindoline corresponding to formula (IIIa):



(IIIa)

in which, independently of one another

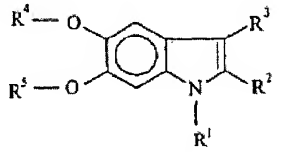
- R^1 is hydrogen, a C_1-C_4 alkyl group or a C_1-C_4 hydroxyalkyl group,
- R^2 is hydrogen or a -COOH group, the -COOH group optionally being present as a salt with a physiologically compatible cation,
- R^3 is hydrogen or a C_1-C_4 alkyl group,
- R^4 is hydrogen, a C_1-C_4 alkyl group or a group -CO-R^6, where R^6 is a C_1-C_4 alkyl group, and
- R^5 is one of the groups mentioned for R^4,

and physiologically compatible salts of these compounds with an organic or inorganic acid.

Particularly preferred derivatives of indoline are 5,6-dihydroxy-indoline, N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline, 5,6-dihydroxy-indoline-2-carboxylic acid and 6-hydroxyindoline, 6-aminoindoline and 4-aminoindoline.

Within this group, particular emphasis is placed on N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxy-indoline, N-butyl-5,6-dihydroxyindoline and, in particular, 5,6-dihydroxy-indoline.

Other particularly suitable precursors of natural hair-dye analogs are derivatives of 5,6-dihydroxyindole corresponding to formula (IIIb):



(IIIb)

in which, independently of one another

- R^1 is hydrogen, a C_1-C_4 alkyl group or a C_1-C_4 hydroxyalkyl group,
- R^2 is hydrogen or a -COOH group, the -COOH group optionally being present as a salt with a physiologically compatible cation,
- R^3 is hydrogen or a C_1-C_4 alkyl group,
- R^4 is hydrogen, a C_1-C_4 alkyl group or a group -CO-R^6, where R^6 is a C_1-C_4 alkyl group, and
- R^5 is one of the groups mentioned for R^4, and
- physiologically compatible salts of these compounds with an organic or inorganic acid.

Particularly preferred derivatives of indole are 5,6-dihydroxyindole, N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole, 5,6-dihydroxyindole-2-carboxylic acid, 6-hydroxyindole, 6-aminoindole and 4-aminoindole.

Within this group, particular emphasis is placed on N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole and, in particular, 5,6-dihydroxyindole.

The indoline and indole derivatives may be used in the colorants according to the invention both as free bases and in the form of their physiologically compatible salts with inorganic or organic acids, for example hydrochlorides, sulfates and hydrobromides. The indole or indoline derivatives are normally present in these colorants in amounts of 0.05 - 10 wt.%, preferably 0.2 - 5 wt.%.

In a further embodiment, it can be preferred according to the invention to use the indoline- or indole derivative in colorants in combination with at least one amino acid or an oligopeptide. The amino acid is advantageously an α-amino acid; quite particularly preferred α-amino acids are arginine, ornithine, lysine, serine and histadine, particularly arginine.

In a further preferred embodiment of the present invention, the inventive hair colorants may comprise, in addition to the inventive dyestuff precursors (FV), one or more substantive dyes for modifying the shades. Substantive dyes are typically nitrophenylenediamines, nitroaminophenols, azo dyes, anthraquinones or indophenols. Preferred substantive dyes are the compounds known under the International names or commercial names HC Yellow 2, HC Yellow 4, HC Yellow 5, HC Yellow 6, HC Yellow 12, Acid Yellow 1, Acid Yellow 10, Acid Yellow 23, Acid Yellow 36, HC Orange 1, Disperse Orange 3, Acid Orange 7, HC Red1, HC Red 3, HC Red 10, HC Red 11, HC Red 13, Acid Red 33, Acid Red 52, HC Red BN, Pigment Red 57:1, HC Blue 2, HC Blue 12, Disperse Blue 3, Acid Blue 7, Acid Green 50, HC Violet 1, Disperse Violet 1, Disperse Violet 4, Acid Violet 43, Disperse Black 9, Acid Black 1 and Acid Black 52 and also 1,4-diamino-2-nitrobenzene, 2-amino-4-nitrophenol, 1,4-bis-(β-hydroxyethyl)-amino-2-nitrobenzene, 3-nitro-4-(β-hydroxyethyl)-aminophenol, 2-(2'-hydroxyethyl)-amino-4,6-dinitrophenol, 1-(2'-hydroxyethyl)-amino-4-methyl-2-nitro-benzene, 1-

amino-4-(2'-hydroxyethyl)-amino-5-chloro-2-nitrobenzene, 4-amino-3-nitrophenol, 1-(2'-ureidoethyl)-amino-4-nitrobenzene, 4-amino-2-nitrodiphenylamine-2'-carboxylic acid, 6-nitro-1,2,3,4-tetrahydroquinoxaline, 2-hydroxy-1,4-naphthoquinone, picramic acid and salts thereof, 2-amino-6-chloro-4-nitrophenol, 4-ethylamino-3-nitrobenzoic acid and 2-chloro-6-ethylamino-1-hydroxy-4-nitrobenzene.

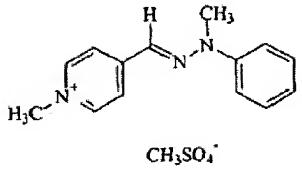
Moreover, according to the invention, the inventive compositions may comprise cationic substantive dyes. Particularly preferred thereby are

(a) cationic triphenylmethane dyestuffs such as, for example, Basic Blue 7, Basic Blue 26, Basic Violet 2 and Basic Violet 14,

(b) aromatic systems substituted by a quaternary nitrogen group such as, for example, Basic Yellow 57, Basic Red 76, Basic Blue 99, Basic Brown 16 and Basic Brown 17 and

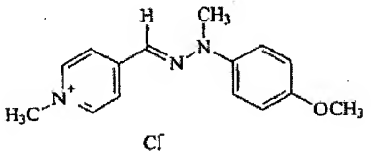
(c) substantive dyestuffs containing a heterocycle with at least one quaternary nitrogen atom, such as, for example, those explicitly referred to in Claims 6 to 11 of EP-A2 998 908.

Preferred cationic substantive dyes of group (c) are, in particular, the following compounds:



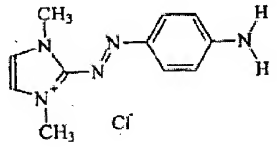
$CH_3SO_4^-$

(DZ1)

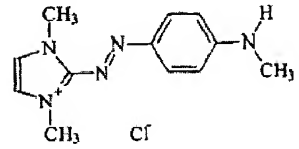


Cl^-

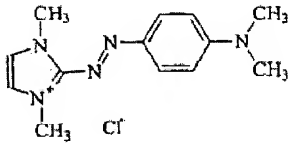
(DZ2)



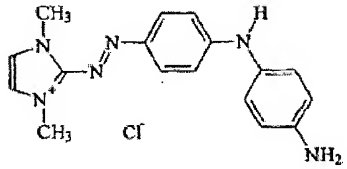
(DZ3)



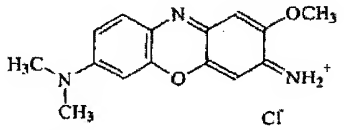
(DZ4)



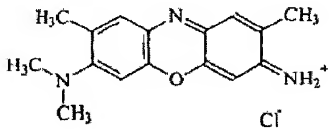
(DZ5)



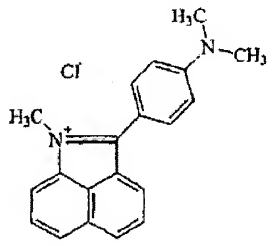
(DZ6)



(DZ7)



(DZ8)



(DZ9)

The compounds corresponding to formulae (DZ1), (DZ3) and (DZ5), which are also known as Basic Yellow 87, Basic Orange 31 and Basic Red 51, are quite particularly preferred cationic substantive dyestuffs of group (c).

According to the invention, the cationic substantive dyestuffs marketed under the name of Arianor® are also quite particularly preferred cationic substantive dyestuffs.

The inventive compositions according to this embodiment preferably comprise the substantive dyes in a quantity of 0.01 to 20 wt.%, based on the total colorant.

The preparations according to the invention may also contain naturally occurring dyestuffs such as, for example, henna red, henna neutral, henna black, camomile blossom, sandalwood, black tea, black alder bark, sage, logwood, madder root, catechu, cedar and alkanet root.

It is not necessary for the oxidation dye precursors or the substantive dyes to each represent homogeneous compounds. Rather, it is possible that as a result of the synthetic procedures for the individual dyestuffs, further components are present in minor amounts in the inventive hair colorants, provided that these do not adversely affect the coloring result, or have to be excluded for other reasons, e.g. toxicological reasons.

With regard to the dyestuffs which can be used in the hair colorants and tints according to the invention, reference is also made expressly to the monograph by Ch. Zviak, The Science of Hair Care, chapter 7 (pages 248-250; substantive dyes), and chapter 8, pages 264-267; oxidation dye precursors), published as volume 7 of the series "Dermatology" (Ed. Ch., Culnan and H. Maibach), Verlag Marcel Dekker Inc., New York, Basle, 1986, and the "European Inventory of Cosmetic Raw Materials", published by the European Commission, available in diskette format from the Bundesverband Deutscher Industrie- und Handelsunternehmen fur Arzneimittel, Reformwaren und Korperpflegemittel e.V., Mannheim.

The colorants according to the invention may also contain any of the known active substances, additives and auxiliaries typical of such formulations. In many cases, the colorants contain at least one surfactant, both anionic and zwitterionic, ampholytic, nonionic and cationic surfactants being suitable in principle. In many cases, however, it has been found to be advantageous to select the surfactants from anionic, zwitterionic or nonionic surfactants. With regard to the preferred surfactant according to the invention, reference should also be made to the previous embodiments.

In a further preferred embodiment of this subject matter of the present invention, the compositions comprise at least one reducing agent. According to the invention, examples of preferred reducing agents are sulfites, ascorbic acid, isoascorbic acid, thiols, thioglycolic acid and its derivatives, sodium thionite, alkali metal citrate salts and N-acetyl-L-cystein. Quite particularly preferred reducing agents are sulfites, particularly sodium sulfite, alkali metal citrate salts, particularly sodium citrate, and N-acetyl-L-cystein. N-acetyl-L-cystein and sodium sulfite are quite particularly preferred reducing agents.

Moreover, the inventive colorants may comprise further active substances, auxiliaries and additives, such as, for example

- cationic polymers like quaternized cellulose ethers, polysiloxanes with quaternary groups, dimethyldiallylammonium chloride polymers, acrylamide-dimethyldiallylammonium chloride copolymers, dimethylamino-ethyl methacrylate-vinyl pyrrolidone copolymers quaternized with diethyl sulfate, vinyl pyrrolidone-imidazolinium methochloride copolymers and quaternized polyvinyl alcohol,
- anionic polymers such as, for example polyacrylic acid, crosslinked polyacrylic acid, vinyl acetate/crotonic acid copolymers, vinyl pyrrolidone/vinyl acetate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinyl ether/maleic anhydride copolymers and acrylic acid/ethyl acrylate/N-tert.butylacrylamide terpolymers,
- structurants, such as maleic acid and lactic acid,
- light stabilizers, in particular derivatized benzophenones, cinnamic acid derivatives and triazines,
- substances for adjusting the pH, such as, for example, typical acids, particularly food acids and bases,
- active substances such as allantoin, pyrrolidone carboxylic acids and their salts as well as bisabolol,
- vitamins, provitamins and vitamin precursors, particularly those of groups A, B_3, B_5, B_6, C, E, F and H,
- plant extracts such as extracts from green tea, oak bark, stinging nettle, hamamelis, hops, camomile, burdock root, horse willow, hawthorn, lime blossom, almond, aloe vera, pine needle, horse chestnut, sandalwood, juniper, coconut, mango, apricot, lemon, wheat, kiwi, melon, orange, grapefruit, sage, rosemary, birch, mallow, lady's smock, creeping thyme, yarrow, thyme, balm, restharrow, coltsfoot, hibiscus, meristem, ginseng and ginger root
- swelling and penetration substances, such as glycerol, propylene glycol monoethyl ether, carbonates, hydrogencarbonates, guanidines and ureas,
- opacifiers, such as latex, styrene/PVP and styrene/acrylamide copolymers
- pearlizing agents, such as ethylene glycol mono- and distearate and PEG-3 distearate,

- anti-corrosives such as optionally hydrated SiO_2 compounds
- stabilizers for hydrogen peroxide and other oxidizing agents.

Concerning further facultative components and their addition quantities, reference is expressly made to the previous embodiments and to the relevant handbooks known to the expert, e.g. Kh. Schrader, Grundlagen und Rezepturen der Kosmetika, 2nd edition. Hüthig Buch Verlag, Heidelberg, 1989.

A third subject of the present invention are two-component agents for coloring keratinous fibers, consisting of

- a first component (K1) comprising at least one dyestuff precursor (FV), and
- a second component (K2) comprising at least one active substance complex (A) consisting of
  - an active substance (A1), selected from sericin and/or sericin hydrolyzates and/or their derivatives and/or their mixtures, and
  - an active substance (A2), selected from fibroin and/or its hydrolyzates and/or its derivatives and/or mixtures thereof,

wherein at least one of the two components comprises at least one amphoteric polymer (AP).

In the scope of a preferred embodiment of this subject matter of the present invention, both components (K1) and (K2) comprise at least one amphoteric polymer (AP). In this case it can be quite particularly preferred that the components (K1) and (K2) comprise the same amphoteric polymer (AP).

The inventive two-component agents are combined immediately prior to their use into a ready-to-use application preparation, which is then applied to the hair.

In the context of this subject matter of the present invention, the actual oxidative coloration of the fibers occurs with oxygen in the air.

Preferably however, a chemical oxidizing agent is added, especially if a lightening effect as well as the coloration of the human hair is desired.

A fourth subject of the present invention is accordingly a three-component agent for the coloration of keratinous fibers, consisting of

- a first component (K1) comprising at least one dyestuff precursor (FV),
- a second component (K2) comprising at least one active substance complex (A) consisting of
  - o an active substance (A1), selected from sericin and/or sericin hydrolyzates and/or their derivatives and/or their mixtures, and
  - o an active substance (A2), selected from fibroin and/or its hydrolyzates and/or its derivatives and/or mixtures thereof, and
- a third component (K3), comprising at least one oxidizing agent,

wherein at least one of the two components (K1) or (K2) comprises at least one amphoteric polymer (AP).

The oxidizing agents can be persulfates, chlorites and particularly hydrogen peroxide or its addition products on urea, melamin as well as sodium borate. In the context of this subject matter of the present invention, the ready-to-use product is obtained by mixing the three components immediately prior to use on the hair.

In the context of fiber coloration, if an extreme lightening of the natural color of the keratinous fibers were required, then a so-called booster would be added to the application preparation made up of colorant cream and oxidizing agent preparation (normally a solution of hydrogen peroxide). For the most part these powdered formulated agents normally contain a solid peroxy-compound as the major component. In principal, the choice of peroxide compound is not limited; typical peroxy-compounds known to those skilled in the art are for example ammonium peroxydisulfate, potassium peroxydisulfate, sodium peroxydisulfate,

ammonium persulfate, potassium persulfate, sodium persulfate, potassium peroxydiphosphate, percarbonates such as magnesium percarbonate, peroxides such as barium peroxide as well as perborates, urea peroxide and melamin peroxide. Among these peroxy-compounds, which may also be used in combination, inorganic compounds are preferred according to the invention. Peroxydisulfates, particularly combinations of at least two peroxydisulfates, are particularly preferred. Recently, however, processes have also been developed in which special ammonium salts and salt combinations were used instead of peroxy-compounds. Explicit reference is made here to EP-609 796A2 and DE-196 30 453A1.

According to the invention, the colorant can also be applied to the hair together with a catalyst, which activates the oxidation of the dyestuff precursor with e.g. oxygen from the air. Such catalysts are e.g. metal ions, iodides, quinones or specific enzymes.

Suitable metal ions are for example Zn^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{4+}, Li^{+}, Mg^{2+}, Ca^{2+} and Al^{3+}. From these, Zn^{2+}, Cu^{2+} and Mn^{2+} are particularly preferred. In principle the metal ions may be used in the form of any physiologically compatible salt or in the form of a complex compound. Preferred salts are the acetates, sulfates, halides, lactates and tartrates. The use of these metal salts can specifically influence both the acceleration of color formation as well as the color nuance.

Suitable enzymes are e.g. peroxidases, which can markedly enhance the effect of minor amounts of hydrogen peroxide. According to the invention, such enzymes are moreover suited to directly oxidize the oxidation dyestuff precursors with oxygen in the air, such as, for example the laccases, or to produce minor quantities of hydrogen peroxide *in situ* and in this manner biocatalytically activate the oxidation of the dyestuff precursors.

Particularly suitable catalysts for the oxidation of the dyestuff precursors are the so-called 2-electron oxido-reductases combined with the specific substrates for them, e.g.

- pyranose-oxidase and e.g. D-glucose or galactose,
- glucose-oxidase and D-glucose,
- glycerol-oxidase and glycerol,
- pyruvate-oxidase and pyruvic acid or its salts,
- alcohol-oxidase and alcohols (MeOH, EtOH),
- lactate oxidase and lactic acid and its salts,
- tyrosinase-oxidase and tyrosine,
- uricase and uric acid or its salts
- choline-oxidase and choline,
- amino acid-oxidase and amino acids.

The compositions/components according to the invention preferably comprise the active substances in a suitable aqueous, alcoholic or aqueous/alcoholic carrier. For hair coloration purposes, such carriers are, for example, creams, emulsions, gels or other foaming solutions that contain surfactants, such as, for example shampoos, foam aerosols or other preparations suitable for application to the hair. It is also conceivable to formulate one or more of the inventive preparations as powders or also as tablets.

In the context of the present invention, the term aqueous alcoholic solutions, is understood to mean aqueous solutions comprising 3 to 70 wt.% of a C_1-C_4 alcohol, particularly ethanol or isopropanol. The inventive compositions may, in addition comprise further organic solvents such as, for example methoxybutanol, benzyl alcohol, ethyl diglycol or 1,2-propylene glycol. Water-soluble organic solvents are preferred.

Each resulting ready-to-use hair coloration preparation should preferably have a pH in the range 6 to 12. The application of the hair coloration composition in a weakly alkaline medium is preferred. The application temperatures may lie

between 15 and 40°C. After a contact time of 5 to 45 minutes, the hair coloration composition is rinsed out and removed from the hair being colored. A rewash with a shampoo is dispensed with if a strongly surfactant-containing carrier, e.g. a color shampoo, has been used.

Particularly with difficultly colorable hair, the preparation, with the dyestuff precursors, can be applied to the hair, but also without prior mixing with the oxidation components. After a contact time of 20 to 30 minutes - where appropriate after an intermediate rinse - the oxidation components are then applied. After a further contact time of 10 to 20 minutes, the hair is then rinsed and if desired reshampooed. In a first variant of this embodiment, in which the prior application of the dyestuff precursors should bring about a better penetration into the hair, the pH of the appropriate composition is adjusted to about 4 to 7. In a second variant, first an air oxidation is aimed for, the applied composition preferably having a pH from 7 to 10. The use of acid-adjusted peroxydisulfate solutions as the oxidizing agent for the subsequent accelerated post oxidation can be preferred.

A fifth subject of the present invention is a process for coloring keratinous fibers wherein one of the inventive compositions is applied to the fibers, left there for a contact time and subsequently rinsed out.

A sixth subject of the invention are cosmetics comprising:

a. the active substance complex (A)
b. and a compound selected from the group of surfactants (E) and/or polymers (G).

Concerning further components of these compositions, reference is made to the above statements.

A seventh subject of the present invention is a process for the treatment of skin or hair, in which a composition with the inventive active substance complex (A),

according to any one of Claims 1 to 7, is applied to the fibers, the composition being rinsed out again if desired, after a contact time of from 1 to 45 minutes.

Examples

All quantities are parts by weight unless otherwise stated.

1 Demonstration of the activity

Comparative experiments were carried out by parting the hair of the test persons down the middle. 5 - 7 ml of the respective active substance solutions were added on each half of the head to the towel-wet hair, i.e. slightly wet hair, and massaged in. The products of Table 1 were tested and evaluated in the half-side test on four models, each with different hair quality, by four trained experts. The criteria used for the evaluation were wet combability, dry combability, wet hair feel, dry hair feel, volume as well as hair gloss.

Table 1: Formulations of the comparative tests:

	Invention (E) in % AS	Comparison 1 (V1) in % AS	Comparison 2 (V2) in %AS
Promois Silk 1000 (determined as ca. 6.5% fibroin hydrolyzate as dry residue in raw material, Interorgana company)	0.029	---	0.04
Sericin (determined as ca. 5.7% sericin as dry residue in raw material, Pentapharm)	0.009	0.004	---
Water	Made up to 100		
Total quantity of active substances	0.038	0.04	0.04
Weight proportion of sericin in the active substance complex	24%	100%	0%

The results are summarized in Table 2. The result is clearly shown that a combination of the inventive active substances A1 and A2 in the active substance complex A gives a markedly synergistic increased effect compared to the effects of the same amounts of active substances used in the individual raw materials.

Table 2: Results of the half-side tests:

	E versus V+ and V2
Wet combability	Better
Dry combability	Better
Wet feel	Better
Dry feel	Better
Gloss	Better
Volume	Better

2 *Application examples*

2.1 *Hair rinsing*

Eumulgin® B2[1]	0.3
Cetyl/stearyl alcohol	3.3
Sericin	0.3
Promois® Silk – 1000	0.7
Isopropyl myristate	0.5
Lamesoft® PO 65[4]	0.5
Dehyquart® A-CA[2]	2.0
Salcare® SC96[5]	1.0
Citric acid	0.4
Gluadin®[6] W40	2.0
Pyridoxine	1.0
Tartaric acid	0.7

Phenonip®[3]	0.8
Water	made up to 100

1. cetylstearyl alcohol + 20EO (INCI name: Ceteareth-20) (COGNIS)
2. trimethylhexadecylammonium chloride ca. 25% active substance (INCI name: Cetronium chloride) (COGNIS)
3. methyl hydroxybenzoate - ethyl hydroxybenzoate - propyl hydroxybenzoate - butyl hydroxybenzoate – phenoxyethanol mixture (ca. 28% active substances; INCI name: phenoxyethanol, methylparaben, ethylparaben, propylparaben, butylparaben) (NIPA)
4. mixture of alkyl polyglycoside and fatty acid monoglyceride (INCI name: coco-glucoside (and) glyceryl oleate)
5. N,N,N-trimethyl-2[(methyl-1-oxo-2-propenyl)oxy]-ethanaminium chloride homopolymer (50% active substance; INCI name: polyquaternium-37 (and) propylene glycol dicaprilate dicaprate (and) PPG-1 Trideceth-6) (ALLIED COLLOIDS)
6. wheat protein hydrolyzate ca. 40% active substance

2.2 Hair rinsing

Eumulgin® B2	0.3
Cetyl/stearyl alcohol	3.3
Isopropyl myristate	0.5
Paraffin oil perliquidum 15 cSt. DAB 9	0.3
Dehyquart® L 80[7]	0.4
Lamesoft® PO 65	1.5
Cosmedia Guar® C261[8]	1.5
Promois® Milk-CAQ[9]	3.0
Citric acid	0.4
Potassium cocoyl hydrolyzed silk	2.0
Hexapeptide-2	0.3
Poly-L-serine	0.5
Phenonip®	0.8
Water	made up to 100

7. bis(cocoylethyl)-hydroxyethyl-methylammonium methosulfate (ca. 76% active substance in propylene glycol; INCI name: dicocoylethyl hydroxyethylmonium methosulfate, propylene glycol) (COGNIS)

8. Guarhydroxypropyltrimethylammonium chloride; INCI name: Guar hydroxypropyl trimonium chloride (COGNIS)

9. INCI name: cocodimonium hydroxypropyl hydrolyzed casein (SEIWA KASEI)

2.3 Hair treatment

Dehyquart® F75[10]	4.0
Cetyl/stearyl alcohol	4.0
Paraffin oil perliquidum 15 cSt. DAB 9	1.5
Dehyquart® A-CA	4.0
Lamesoft® PO 65	1.0
Salcare® SC96	1.5
Sericin	0.1
Promois silk 1000	0.4
D/L-isoleucine	2.5
Glyoxylic acid	0.5
Amisafe-LMA-60®[11]	1.0
Gluadin® W 20[12]	3.0
Germall® 115[13]	1.0
Citric acid	0.15
Phenonip®	0.8
Water	made up to 100

[10] Fatty alcohol-methyltriethanolammonium methyl sulfate dialkylester mixture (INCI name: Distearoylethyl Hydroxyethylmonium Methosulfate, Cetearyl Alcohol) (COGNIS)

[11] INCI name: Hydroxypropyl Arginine Lauryl/Myristyl Ether HCl (Ajinomoto)

[12] Wheat protein hydrolyzate (20 % active substance in water; INCI name: Aqua (and) Hydrolyzed Wheat Protein (and) Sodium Benzoate (and) Phenoxyethanol (and) Methylparaben (and) Propylparaben) (COGNIS)

[13] INCI name: Imidazolidinyl Urea (Sutton Laboratories)

2.4 Hair treatment

Dehyquart® L80	2.0
Cetyl/stearyl alcohol	6.0
Paraffin oil *perliquidum* 15 cSt. DAB 9	2.0
Rewoquat® W75[14]	2.0
Cosmedia Guar® C261	0.5
Lamesoft® PO65	0.5
Sepigel®305[15]	3.5
Honeyquat® 50[16]	1.0
Gluadin® WQ	2.5
Gluadin® W 20	3.0
Hydrolyzed sericine	0.8
L-glycine	0.4
L-alanyl-L-proline	1.0
L-tyrosine	0.2
Citric acid	0.15
Phenonip®	0,8
Water	made up to 100

[14] 1-methyl-2-nortallowalkyl-3-tallow acid amidoethylimidazolinium methosulfate (ca. 75 % active substance in propylene glycol; INCI name: Quaternium-27, Propylene Glycol) (WITCO)

[15] Copolymer of acrylamide und 2-acrylamido-2-methylpropanesulfonic acid (INCI name: Polyacrylamide (and) C_{13}-C_{14} Isoparaffin (and) Laureth-7) (SEPPIC)

[16] INCI name: Hydroxypropyltrimonium Honey (BROOKS)

2.5 Hair treatment

Dehyquart® F75	0.3
Salcare® SC 96	5.0
Gluadin® WQ	1.5

Lamesoft® PO 65	0.5
Dow Corning® 200 Fluid, 5cSt.[17]	1.5
Gafquat® 755N[18]	1.5
Poly-D/L-alanine	1.5
Serine	0.1
Glycine methyl ester	0.5
Tyrosine methyl ester	0.2
Sericin	0.2
Biodocarb® [19]	0.02
Perfume oil	0.25
Water	made up to 100

17. Polydimethylsiloxane (INCI name: Dimethicone) (DOWCORNING)

18. Dimethylaminoethylmethacrylate-vinyl pyrrolidone copolymer, quaternized with diethyl sulfate (19 % active substance in water; INCI name: Polyquaternium-11) (GAF)

19. 3-Iodo-2-propynyl-n-butylcarbamate (INCI name: Iodopropynyl Butylcarbamate) (MILKER &GRÜNING)

2.6 Hair Treatment

Sepigel® 305	5.0
Dow Corning® Q2-5220[20]	1.5
Promois® MilkQ[21]	3.0
Lamesoft® PO 65	0.5
Polymer P1 according to DE 3929173	0.6
Genamin® DSAC[22]	0.3
D/L-Methionin-S-Methylsulfonium chloride	1.8
Hydrolyzed Sericin	0.5
Promois® Silk 1000	1.0
Phenonip®	0.8
Perfume oil	0.25
Water	made up to 100

20. Silicone-glycol-copolymer (INCI name: Dimethicone Copolyol) (DOW

CORNING)

21. INCI name: Hydroxypropyltrimonium Hydrolyzed Casein ca. 30% active substance (SEIWA KASEI)

22. Dimethyldistearylammonium chloride (INCI name: Distearyldimonium Chloride) (CLARIANT)

2.7 Shampoo

Texapon® NSO[23]	40.0
Dehyton® G[24]	6.0
Polymer JR400®[25]	0.5
Cetiole HE[26]	0.5
Ajidew® NL 50[27]	1.0
Lamesoft® PO 65	3.0
Sericin	0.8
Promois® Silk 1000	2.0
Gluadine® WQT[26]	2.5
Gluadin® W 20	0.5
Panthenol (50%)	0.3
Casein	2.0
Vitamin E	0.1
Vitamin H	0.1
Glutamic acid	0.2
Citric acid	0.5
Sodium benzoate	0.5
Perfume	0.4
NaCl	0.5
Water	made up to 100

23. Sodium laurylether sulfate ca. 28% active substance (INCI name: Sodium Laureth Sulfate) (COGNIS)

24. INCI name: Sodium Cocoamphoacetate, ca. 30% active substance in water) (COGNIS)

25. Quaternized hydroxyethyl cellulose (INCI name: Polyquaternium-10) (UNION CARBIDE)
26. Polyol-Fatty acid ester (INCI name: PEG-7 Glyceryl Cocoate) (COGNIS)
27. Sodium salt of 2-pyrrolidinone-5-carboxylic acid (50% active substance: INCI name: Sodium PCA) (AJINOMOTO)
28. INCI name: Hydroxypropyltrimonium Hydrolyzed Wheat Protein (COGNIS)

2.8 Shampoo

Texapon® NSO	43.0
Dehyton® K[29]	10.0
Plantacare® 1200 UP[30]	4.0
Lamesoft® PO 65	2.5
Euperlan® PK 3000[31]	1.6
Arquad® 316[32]	0.8
Polymer JR® 400	0.3
Gluadin® WQ	4.0
Lauryldimopnium hydroxypropyl hydrolyzed silk	3.0
Sodium lauroyl hydrolyzed silk	3.0
Sericin	10.0
Lactic acid	0.5
Hydrolupin® AA[33]	0.5
Malic acid	0.5
Glucamate®DOE 120[33]	0.5
Sodium chloride	0.2
Water	made up to 100

29. INCI name: Cocamidopropyl Betaine ca. 30% active substance (COGNIS)
30. C 12 - C 16 Fatty alcohol glycoside ca. 50% active substance (INCI name: Lauryl Glucoside) (COGNIS)
31. Liquid dispersion of pearlescent substances and amphosurfactant (ca. 62 % active substance; CTFA name: Glycol Distearate (and) Glycerin (and) Laureth-4 (and) Cocoamidopropyl Betaine) (COGNIS)
32. Tri-C_{18}-alkylmethylammonium chloride (AKZO)

[33] Amino acid mixture from the total hydrolysis of lupine protein, (INCI name: Lupine Amino Acids) (CRODA)

[34] Ethoxylated methyl glucoside dioleate (CTFA name: PEG-120 Methyl Glucose Dioleate) (AMERCHOL)

2.9 Shampoo

Texapon® N 70[35]	21.0
Plantacare® 1200 UP	8.0
Lamesoft® PO 65	3.0
Gluadine® WQ	1.5
Promoise® Silk 1000	15.0
Sericin	10.0
Cutina® EGMS[36]	0.6
Honeyquat® 50	2.0
Ajidew® NL 50	2.8
Antil® 141[37]	1.3
Crolastin®[38]	1.0
Sodium chloride	0.2
Magnesium hydroxide	to pH 4.5
Water	made up to 100

[35] Sodium laurylether sulfate with 2 mol EO ca. 70% active substance (INCI name: Sodium Laureth Sulfate) (COGNIS)

[36] Ethylene glycol monostearate (ca. 25-35% monoester, 60-70% diester; INCI name: Glycol Stearate) (COGNIS)

[37] Polyoxyethylene-propylene glycol dioleate (40% active substance; INCI name: Propylene Glycol (and) PEG-55 Propylene Glycol Oleate) (GOLDSCHMIDT)

[38] Elastine hydrolyzate (INCI name: Hydrolyzed Elastin) (CRODA)

2.10 Shampoo

Texapon® K 14 S[39]	50.0
Dehyton® K	10.0

Plantacare® 818 UP[40]	4.5
Lamesoft® PO 65	2.0
Potassium Cocoyl Hydrolyzed Silk	5.0
Palmitoyl Pentapeptide-2	2.5
Polymer P1, according to DE 39 29 973	0.6
Cutina® AGS[41]	2.0
D-Panthenol	0.5
Glucose	1.0
Hydrosesame® AA[42]	0.8
Salicylic acid	0.4
Sodium chloride	0.5
Gluadin® WQ	2.0
Water	made up to 100

39. Sodium laurylmyristylether sulfate ca 28% active substance (INCI name: Sodium Myreth Sulfate) (COGNIS)

40. C 8 - C 16 Fatty alcohol glycoside ca. 50% active substance (INCI name: Coco Glucoside) (COGNIS)

41. Ethyleneglycol stearate (ca. 5-15% monoester, 85-95% diester; INCI name: Glycol Distearate) (COGNIS)

42. INCI name: Water (and) Sesame Amino Acids (CRODA)

2.11 Hair Treatment

Celquat® L200[43]	0.6
Luviskol® K30[44]	0.2
D-Panthenol	0.5
Polymer P1, according to DE 39 29 973	0.6
Dehyquart® A-CA	1.0
Lamesoft® PO 65	0.5
Hydrosoy® 2000[45]	1.0
Aspartic acid	0.3
Acetyl Hexapeptide-3	2.0
Promois® Silk 1000	5.0

Gluadin® W 40	1.0
Natrosol® 250 HR[46]	1.1
Gluadin® WQ	2.0
Water	made up to 100

[43] Quaternized cellulose derivative (95 % active substance; CTFA name: Polyquaternium-4) (DELFT NATIONAL)

[44] Polyvinyl pyrrolidone (95 % active substance; CTFA name: PVP) (BASF)

[45] Protein hydrolyzate of Soya (INCI name: Hydrolyzed Soy Protein) (CRODA)

[46] Hydroxyethyl cellulose (AQUALON)

2. 12 Colorant Creams

C_{12-18} Fatty alcohol	1.2
Lanette® O[47]	4.0
Eumulgin® B 2	0.8
Cutina® KD 16[48]	2.0
Lamesoft® PO 65	4.0
Sodium sulfite	0.5
L(+)ascorbic acid	0.5
Ammonium sulfate	0.5
1,2-Propylene glycol	1.2
PolymerJR® 400	0.3
p-Aminophenol	0.35
p-Toluylenediamine	0.85
2-Methylresorcinol	0.14
6-Methyl-m-aminophenol	0.42
Cetiol® OE[49]	0.5
Honeyquat® 50	1.0
Ajidew® NL 50	1.2
Gluadin® WQ	1.0
Crosilk Liquid®[50]	0.5
Promois® Silk 1000	0.5

Sericin	0.3
Ammonia	1.5
Water	made up to 100

47. Cetylstearyl alcohol (INCI name: Cetearyl alcohol) (COGNIS)

48. Self-emulsionizing mixture of mono/di glycerides of higher saturated fatty acids with potassium stearate (INCI name: Glyceryl Stearate SE) (COGNIS)

49. Di-n-octyl ether (INCI name: Dicaprylyl Ether) (COGNIS)

50. Mixture of amino acids from the total hydrolysis of silk proteins (INCI name: Silk Amino Acids) (CRODA)

2.13 Developer Dispersion for Colorant Cream 2.12

Texapon® NSO	2.1
Hydrogen peroxide (50% conc.)	12.0
Turpinal® SL[51]	1.7
Latekoll® D[52]	12.0
Lamesoft® PO65	2.0
Gluadin® WQ	0.3
Salcare® SC96	1.0
Aspartic acid	0.1
Sericine	0.2
Promois® Silk 1000	0.4
Crolastin®	0.8
Water	made up to 100

51. 1-Hydroxyethane-1,1-diphosphonic acid (60% active substance; INCI name Etidronic acid) (COGNIS)

52. Acrylic ester-methacrylic acid copolymer (25% active substance) (BASF)

2.14 Shading Shampoo

Texapon® N 70	14.0
Dehyton® K	10.0
Akypo® RLM 45 NV[53]	14.7

Plantacare® 1200 UP	4.0
Lamesoft® PO 65	3.0
Polymer P1, according to DE 39 29 973	0.3
Cremophor® RH 40[54]	0.8
Poly-L-Serine	0.3
Hydrolyzed Sericin	0.3
Hydroxypropyltrimonium Hydrolyzed Silk	3.0
Benzoic acid	0.3
Poly-L-Proline	0. 3
Dyestuff C.I. 12 719	0.02
Dyestuff C.I. 12 251	0.02
Dyestuff C.I. 12 250	0.04
Dyestuff C.I. 56 059	0.03
Conservation	0.25
Perfume oil	q. s.
Eutanol® G[55]	0.3
Gluadin® WQ	1.0
Honeyquat® 50	1.0
Salcare® SC 96	0.5
Water	made up to 100

[53] Lauryl alcohol+4,5 ethylene oxide-acetic acid sodium salt (20.4 % active substance) (CHEM-Y)

[54] Castor oil, hydrogenated + 45 ethylene oxide (INCI name: PEG-40 Hydrogenated Castor Oil) (BASF)

[55] 2-Octyldodecanol (Guerbet-Alcohol) (INCI name: Octyldodecanol) (COGNIS)

2.15 Permanent Waving Cream

Waving cream

Plantacare® 810 UP[56]	5.0
Thioglycolic acid	8.0
Turpinal® SL	0.5

Ammonia (25% conc.)	7.3
Ammonium carbonate	3.0
Cetyl/stearyl alcohol	5.0
Lamesoft® PO 65	0.5
Guerbet alcohol	4.0
Salcare® SC 96	3.0
Gluadin® WQ	2.0
Hydrolyzed Sericin	0.3
Hydroxypropyltrimonium Hydrolyzed Silk	1.0
Glutaric acid	0.2
Hydrotriticum® 2000[57]	0.5
Perfume oil	q. s.
Water	made up to 100

[56] C_8-C_{10} alkyl glucoside with oligomerization degree of 1.6 (ca. 60% active substance) (COGNIS)

[57] Wheat protein hydrolyzate (INCI name: Hydrolyzed Wheat Protein) (CRODA)

2.16 Fixing solution

Plantacare® 810 UP	5.0
Hydrogenated castor oil	2.0
Lamesoft® PO 65	1.0
Potassium bromate	3.5
Nitrilotriacetic acid	0.3
Citric acid	0.2
Merquat® 550[58]	0.5
Hydagen® HCMF[59]	0.5
Tartaric acid	0.5
Gluadine WQ	0.5
Cocodimonium Hydroxypropyl Silk Amino Acids	0.3
Hydrolyzed Sericin	0.1
D/L-Methionine-S-methylsulfonium chloride	0.3

Perfume oil	q. s.
Water	made up to 100

[58] Dimethyldiallylammonium chloride-acrylamide copolymer (8 % active substance ; INCI name: Polyquarternium 7) (MOBIL OIL)

[59] Chitosan Powder (INCI name: Chitosan) (COGNIS)

3 Further Comparative Experiments

3.1 Preparation of the Formulations

The following formulations were prepared:

3.1.1 Care Components with Silk Proteins

Raw Material	Amount in wt.%
Sericine	4.4
Promois® Silk 1000	7.2
D&C Red 33[60]	q.s.
D&C Yellow 10[61]	q.s.
Ascorbic acid	0.2
Sodium sulfite	0.2
Sodium benzoate	0.3
Sodium salicylate	0.3
Natrosol® 250HR	1.2
Aqueous KOH solution (50% conc.)	0.2
Citric acid	to pH 5.0
Water	to 100

[60] Disodium salt of 5-amino-4-hydroxy-3-phenylazo-2,7-naphthalene disulfonic acid (INCI name: CI=17200)

[61] (INCI name: CI=47005 (Yellow 10))

3.1.2. Care Components with Silk Proteins and Amphoteric Polymer

Raw Material	Amount in wt.%
Sericine	4.4
Promois® Silk 1000	7.2
D&C Red 33	q.s.
D&C Yellow 10	q.s.
Ascorbic acid	0.2
Sodium sulfite	0.2
Sodium benzoate	0.3
Sodium salicylate	0.3
Polymer W37194[62]	1.25
Natrosol® 250HR	1.2
Aqueous KOH solution (50% conc.)	0.2
Citric acid	to pH 5.0
Water	to 100

[62] ca. 20 wt.% active substance in water; INCI name: acrylamidopropyltrimonium chloride/acrylates copolymer (Stockhausen)

3.1.3. Dyestuff preparation

Raw Material	Amount in wt.%
Texapon® K 14 S 70 C[63]	2.8
Akypo Soft® 45 NV[64]	10.0
Hydrenol® D[65]	5.5
Lorol® technical[66]	2.0
Lamesoft® PO 65	2.0
Eutanol® G	1.0
Polymer W37194	3.75

Eumulgin® B1[67]	0.5
Eumulgin® B2	0.5
p-Tolulylenediamine sulfate	0.4
m-Aminophenol	0.01
4-Chlororesorcinol	0.06
2-Methylresorcinol	0.02
Resorcinol	0.1
Ammonium sulfate	0.7
Ascorbic acid	0.4
Sodium sulfite	0.5
Turpinal® SL	0.2
Perfume oil	0.3
Water glass 40/42[68]	0.5
Water	to 100
Aqueous NH_4OH solution	to pH 10.5

63. Sodium salt of laurylmyristyl ether sulfate (ca. 68% to 73% active substance content; INCI name: Sodium Myreth Sulfate) (COGNIS)
64. Sodium salt of lauryl alcohol-4,5-EO-acetic acid (min. 21% active substance content; INCI name: Sodium Laureth-6 Carboxylate) (Chem-Y)
65. C_{16-18} Fatty alcohol (INCI name: Cetearyl alcohol) (Cognis)
66. C_{12-18} Fatty alcohol (INCI name: Coconut alcohol) (Cognis)
67. C_{16-18} Fatty alcohol with ca. 12-EO units (INCI name: Ceteareth-12) (Cognis)
68. ca. 40% active substance (INCI name: Sodium silicate) (HENKEL)

3.1.4 Oxidizing Agent preparation

Raw Material	Amount in wt.%
Dipicolinic acid	0.1
Sodium pyrophosphate	0.03

Turpinal® SL	1.5
Texapon® NSO[69]	2.0
Dow Corning® DB 110 A[70]	0.07
Aculyn® 33[71]	15.0
Hydrogen peroxide (50% conc.)	12.0
Water	to 100
Aqueous NH_4OH solution	to pH 2

69. Sodium salt of laurylether sulfate (INCI name: Sodium Laureth Sulfate, ca. 26.5% active substance) (Cognis)

70. nonionic silicone emulsion (INCI name: Dimethicone, ca. 10% active substance) (Dow Corning)

71. Acid-containing, crosslinked acrylic copolymer (INCI name: Acrylates Copolymer, ca. 28% active substance) (Rohm & Haas)

3.2 Coloration of Strands

The coloration creams F1 to F3 according to Table 3 were mixed in a 1:1 ratio with the oxidizing agent preparation (see point 3.1.4). 8g of each resulting application preparation were applied to 20 natural hair strands (2g. Alkinco 6634, just bleached with the commercial product Poly Blonde® Medium) and left there for 30 minutes at room temperature. Subsequently, the hair was thoroughly rinsed out with water.

Immediately after rinsing, the wet combability of the strands was determined. In the scope of these measurements the comb resistance is determined, i.e. the force required to pull a standard comb through the strands of hair. Each measured value of the strands before coloration (0% reduction in wet combability) was taken as the reference. The results are summarized in Table 3.

Table 3

Coloration Cream	Composition	Reduction in Wet Combability
F1 (according to the invention)	10 ml care components with silk proteins (see point 3.1.1) and 240 ml coloration cream (see point 3.1.3)	57%
F2 (according to the invention)	10 ml care components with silk proteins and amphoteric polymer (see point 3.1.2) and 240 ml coloration cream (see point 3.1.3)	69%
F3 (not according to the invention)	250 ml coloration cream (see point 3.1.3)	48%

The results clearly show that the inventive formulations with silk proteins and an amphoteric polymer (F1 and F2) are clearly superior to the comparative formulation with amphoteric polymer alone (F3), as far as concerns wet combability (greater reduction in the wet combing force).

3.3 Coloration using test persons

In addition, the inventive coloration creams F1 and F2 were tested against the coloration cream F3 using the half-side test in the hair studio. For this, 40 models each had their hair parted into two sides. One side of the hair was treated with the inventive formulation (60 ml F1 or 60 ml F2 each mixed with 30ml oxidizing agent preparation according to point 3.1.4), the other side with the comparative formulation (60 ml F3 mixed with 60 ml oxidizing agent preparation according to point 3.1.4). Otherwise the test persons' hair was treated identically. The coloration took place at room temperature over 30 minutes. Finally the hair was thoroughly rinsed with water and dried. 3 people of

the expert group carried out the evaluation independently of each other. The evaluations are summarized in Table 4.

Table 4

Tested Property	F1	F2
Wet combability	++	++
Brightness	+	++
Dry combability	(+)	(+)

The claims defining the invention are as follows:

1. Cosmetic preparations comprising an active ingredient complex (A) consisting of:

(a) an active ingredient (A1) which is chosen from sericin and/or derivatives thereof and/or mixtures thereof, and

(b) an active ingredient (A2) which is chosen from fibroin and/or derivatives thereof and/or mixtures thereof.

2. Cosmetic preparations according to claim 1, wherein a compound chosen from the group of surfactants (E) and/or the group of polymers (G) is also present.

3. Cosmetic preparations according to claim 2, wherein the surfactant is chosen from the group of cationic surfactants.

4. Cosmetic preparations according to claim 2, wherein the polymer is chosen from the group of cationic and/or amphoteric polymers.

5. Agent for dyeing keratin fibres comprising, in a cosmetically acceptable carrier, an active ingredient complex (A) according to claim 1, and

(a) at least one dye precursor (DP) and

(b) an amphoteric polymer (AP).

6. Two-component agent for dyeing keratin fibres consisting of a first component (C1) comprising at least one dye precursor (DP), and a second component (C2) comprising at least one active ingredient complex (A) according to claim 1, wherein at least one of the two components comprises at least one amphoteric polymer (AP).

7. Three-component agent for dyeing keratin fibres consisting of a first component (C1) comprising at least one dye precursor (DP), a second component (C2) comprising at least one active ingredient complex (A) according to claim 1 and a third component (C3) comprising at least one oxidizing agent, wherein at least one of the two components (C1) or (C2) comprises at least one amphoteric polymer (AP).

8. Agent according to any one of claims 4 to 7, wherein the amphoteric polymer (AP) is essentially composed of:

(a) monomers with quaternary ammonium groups of the general formula (I),

$$R^1\text{-}CH{=}CR^2\text{-}CO\text{-}Z\text{-}(C_nH_{2n})\text{-}N^{(+)}R^3R^4R^5A^{(-)} \quad (I)$$

where R^1 and R^2, independently of one another, are hydrogen or a methyl group,

R^3, R^4 and R^5, independently of one another, are alkyl groups having 1 to 4 carbon atoms,

Z is an NH group or an oxygen atom,

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n is an integer from 2 to 5,

and $A^{(-)}$ is the anion of an organic or inorganic acid, and

(b) monomeric carboxylic acids of the general formula (II),

R^6-CH=CR^7-COOH (II)

where R^6 and R^7, independently of one another, are hydrogen or methyl groups.

9. Agent according to claim 8, wherein R^3, R^4 and R^5 are methyl groups.

10. Agent according to any one of claims 8 or 9, wherein Z is an NH group.

11. Agent according to any one of claims 8 to 10, wherein the monomeric carboxylic acid of formula (II) is acrylic acid.

12. Agent according to any one of claims 5 to 11, wherein at least one of the two active ingredients (A1) or (A2) is largely present in its native form.

13. Agent according to any one of claims 5 to 12, wherein the dye precursor (DP) present is at least one developer component and/or coupler component.

14. Agent according to any one of claims 5 to 13, wherein the dye precursor (DP) present is at least one indole derivative and/or indoline derivative.

15. Agent according to any one of claims 5 to 14, wherein said agent also comprises at least one direct dye.

16. Agent according to any one of claims 5 to 15, wherein said agent comprises at least one nonionogenic surfactant.

17. Agent according to claim 16, wherein the nonionogenic surfactant is an alkyl polyglucoside.

18. Agent according to any one of claims 5 to 17, wherein said agent comprises at least one reducing agent.

19. Method of dyeing keratin fibres wherein one of the agents according to any one of claims 5 to 18 is applied to the fibres, left there for a contact time and then rinsed off.

20. Use of a cosmetic preparation according to any one of claims 1 to 4 for the cleaning and/or care of skin and hair.

21. Use of a cosmetic preparation according to any one of claims 1 to 4 for the restructuring of keratin fibres, in particular human hair.

22. Method of treating skin or hair in which a preparation according to any one of claims 1 to 4 is applied to said skin or hair, the preparation being rinsed out again after a contact time of from 1 to 45 minutes.

23. Dyed keratin fibres produced in accordance with the method of claim 19.

24. Cosmetic preparations according to claim 1, substantially as hereinbefore described with reference to any one of the examples but excluding the comparative examples.

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